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# Cocaine and cannabinoids in the atmosphere of Northern Europe cities, comparison with Southern Europe and wastewater analysis

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## Abstract

This study reports the first investigation of atmospheric illicit drug concentrations in Northern Europe using measurements of cocaine and cannabinoids in Amsterdam, London and Stockholm. Further, these measurements were compared to those made in Rome to explore the geographical and inter-city variability. Co-located measurements of atmospheric particulate mass and PAHs were used to help describe and interpret the illicit drug measurements with respect to atmospheric dispersion. Cocaine concentrations ranged from 0.03 to 0.14 ng/m$^3$ in Amsterdam, from 0.02 to 0.33 ng/m$^3$ in London and were below quantification limit (3 pg/m$^3$) in Stockholm. Cannabinol was the only cannabinoid molecule detected in the three cities. During this campaign, London reported the highest concentrations of cocaine and meaningful differences were detected between the urban background and city centre London sites. Mean cocaine concentrations measured in Amsterdam during March 2011 were also compared with those measured simultaneously in eight Italian cities. The cocaine concentration in Amsterdam was comparable to that measured at an urban background in Milan and at a densely populated site in Florence. Although correlating atmospheric concentrations directly with drug prevalence is not possible using current data, links between concentrations of cocaine and estimates of abuse prevalence assessed by the more routinely used wastewater analysis were also examined. A statistically significant correlation was found between the two sets of data ($R^2$= 0.66; p = 0.00131). Results confirmed that meteorology, population rate and habits of consumption influence the atmospheric concentrations of drugs. If these confounding factors were better controlled for, the techniques described here could became an easy and cost effective tool to index the impact of cocaine abuse in the area; especially where local hot spots need to be identified.

Highlights

The presence of illicit drugs in the air of Amsterdam, London and Stockholm was investigated. The highest concentration of cocaine was found in London.

Cannabinoid concentrations were lower in Northern than in Southern Europe.

Air concentrations of cocaine and abuse estimates by wastewater analysis were compared.

Population density and abuse fluctuations influence the air load/abuse estimate correlation.

# Cocaine and cannabinoids in the atmosphere of Northern Europe cities, comparison with Southern Europe and wastewater analysis

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**Keywords: Illicit drugs; cocaine; atmosphere, $PM_{10}$; wastewater analysis.**

## Abstract

This study reports the first investigation of atmospheric illicit drug concentrations in Northern Europe using measurements of cocaine and cannabinoids in Amsterdam, London and Stockholm. Further, these measurements were compared to those made in Rome to explore the geographical and inter-city variability. Co-located measurements of atmospheric particulate mass and PAHs were used to help describe and interpret the illicit drug measurements with respect to atmospheric dispersion. Cocaine concentrations ranged from 0.03 to 0.14 ng/m$^3$ in Amsterdam, from 0.02 to 0.33 ng/m$^3$ in London and were below quantification limit (3 pg/m$^3$) in Stockholm. Cannabinol was the only cannabinoid molecule detected in the three cities. During this campaign, London reported the highest concentrations of cocaine and meaningful differences were detected between the urban background and city centre London sites. Mean cocaine concentrations measured in Amsterdam during March 2011 were also compared with those measured simultaneously in eight Italian cities. The cocaine concentration in Amsterdam was comparable to that measured at an urban background in Milan and at a densely populated site in Florence. Although correlating atmospheric

concentrations directly with drug prevalence is not possible using current data, links between concentrations of cocaine and estimates of abuse prevalence assessed by the more routinely used wastewater analysis were also examined. A statistically significant correlation was found between the two sets of data ($R^2$= 0.66; p = 0.00131). Results confirmed that meteorology, population rate and habits of consumption influence the atmospheric concentrations of drugs. If these confounding factors were better controlled for, the techniques described here could became an easy and cost effective tool to index the impact of cocaine abuse in the area; especially where local hot spots need to be identified.

## 1. Introduction

In recent years, environmental research has gained an increasing interest in new classes of compounds, comprising illicit psychotropic substances (PS). Although the potency of the biological effects of illicit drugs is recognized, very little is known about their potential harmful impact on the environment (Daughton, 2011). Most investigations have focused on developing tools to evaluate the abuse prevalence by measuring levels of drug residuals in wastewater (Zuccato et al., 2005; Thomas et al., 2012; Mastroianni et al., 2013; Ort et al., 2014; Castiglione et al. 2014 ). Traces of illicit substances have also been found worldwide in surface and drinking waters (Seabra Pereira et al., 2016; van der Aa et al., 2013; Huerta-Fontela et al., 2008) and in sediments and sludges (Álvarez-Ruiz et al., 2015). In this context the ambient atmospheric concentrations have been less well studied despite evidence of cocaine presence in the atmospheric particulate being reported since 1998 (Hannigan et al., 1998). Acute health risk associated with exposure to typical ambient concentrations of illicit drugs has been regarded as negligible (Viana et al., 2010). Nonetheless, the occurrence of illicit drugs in the air merits concern, taking into account that the atmosphere is a key pathway of dispersion both at local and global scale, and the risks posed by chronic exposure to these substances are completely unknown (Mastroianni et al., 2015). This issue is even more important when considering that dedicated investigations have reported that indoor air (houses, offices, primary schools and shops) can be more contaminated by illicit drugs than ambient air (Cecinato et al. 2014, 2016; Bianchi et al., 2014) even where drugs are not consumed. To date little information exists at this regard (McKenzie et al. 2013), but this phenomenon is expected to be accentuated at locations close to drug abuse or manufacture. In fact, cases of positive response to bioassays have been reported both in children and adults even in the absence of direct drug consumption (Kidwell et al. 1997; De Giorgio et al. 2004; Garcia-Bournissen et al 2009; Pichini et al. 2014). In ambient air the highest concentrations of these substances have been reported from spot measurements carried out in Latin America. Cocaine concentrations as high as 17 ng/$m^3$ were

found in Mexico City, and 3.3 ng/m$^3$ in Santiago De Chile (Cecinato et al. 2016). Cocaine was not found in Algeria, both in Algiers and surrounding areas (Ladji et al. 2009; Moussaoui et al. 2013), while traces of cannabinoids were detected. In Europe, some measurements have been made in Oporto, Portugal, and Pančevo, Serbia, but most have been made in Italy and Spain (Cecinato et al., 2009, 2010, 2012; Postigo et al., 2009; Viana et al., 2010, 2011; Mastroianni et al., 2015). In Italy, a number of localities have been investigated for cocaine and three important cannabinoids, i.e. $\Delta^9$-tetrahydrocannabinol (THC), cannabinol (CBL) and cannabidiol (CBD) (Balducci et al., 2009). In Spain, only three cities have been investigated, but a wider range of substances were studied, including native species, by-products and metabolites (e.g., amphetamines, heroin, cocaethylene, ecstasy, benzoylecgonine, 6-acetylmorphine). This study reports the first atmospheric measurements of cocaine and cannabinoids carried out in London, Stockholm and Amsterdam. Wide differences in meteorological and social contexts, as well as in the drug abuse prevalence, characterize the northern European cities studied; differences also exist between them and the southern European cities so far investigated. From this perspective, the first aim of this study is to provide new information on the variability of the ambient concentration of illicit drugs which reflect the differences between these cities. The second aim is to investigate the possible associations between the atmospheric concentrations and the abuse rate in the area detected there.

The concentration of illicit drugs in the atmosphere is controlled by meteorological dispersion, and little is known about drug suspension and transport from sources to the measurement locations. Using ambient concentration measurements of illicit drugs for consumption estimates is therefore unreliable using the current, limited datasets and significant challenges exist to control for variability in atmospheric dispersion. Nonetheless, studies conducted so far provide evidence that this approach can capture differences among geographical localities, locations or zones within a given area, as well as time variations from a few days to consecutive years (Cecinato et.al., 2014). Therefore, measuring illicit drug concentrations in the air could potentially be applied as a new tool to identify local hot spots, which can be associated with consumption, trafficking and manufacture of substances. Recent studies suggest cocaine may be feasible for this purpose. In fact, cocaine is overall associated to the particulate phase (Cecinato and Balducci 2007) and its determination in the PM accounts for total amount in the air. Although no specific studies have been carried out to assess the stability of illicit drugs in the atmosphere, the relative stability of cocaine seems to be inferred by its seasonal behavior, which looks analogous to that of the PM (Perrino et al. 2001; Hu et al., 2011; Kelly et al., 2016), and the winter/summer concentration ratios for cocaine and $PM_{2.5}$ were broadly similar. For instance, in Rome, taking in account 11 sites, ratios as high as 2.1 ± 1.2 and 2.5 ± 0.9, respectively, were observed for cocaine and $PM_{2.5}$. On the contrary cannabinoids (the other

extensively investigated class) have been shown to be markedly less stable showing a reduction of concentration (Cecinato et al., 2012, 2014).

The determination of cocaine and cannabinoids in the atmosphere of Northern Europe cities allowed us to further investigate links between ambient concentration and the drug addiction phenomenon. Accepting that the current knowledge is not advanced enough to quantify usage rates using ambient samples, these measurements may allow an indexing system of illicit drug prevalence to be developed using the existing sampling infrastructure available in all cities. To investigate this, atmospheric illicit drug concentrations were compared between London, Amsterdam and Rome in March 2013 as well as concentrations measured in Amsterdam and eight Italian cities in 2011. This allowed the influence of meteorology and population habits on the illicit drug concentrations to be examined.

The psychotropic compounds nicotine (NIC) and caffeine (CAF) (reported in the text as licit drugs) and polycyclic aromatic hydrocarbons (PAH) were monitored in addition, to provide insights into the characteristics of the sites and eventual peculiarities in the behaviour of illicit drugs (cocaine and cannabinoids). The improvement of the existing illicit drug concentration database, obtained through this study, allowed an examination of the concentrations of atmospheric cocaine over Northern and Southern Europe cities in the light of the drug prevalence in the respective countries. Measurements were also compared to estimates of collective consumption obtained through analysis of drug residuals in wastewater. The effectiveness of this methodology in assessing drug abuse prevalence is ascertained, and the comparison between the outcomes of the two types of study provides important information to verify if the illicit drugs impact over a certain area can be indexed through measurements in the air.

## 2. Experimental

### *2.1. Sites and periods of sampling*

In Amsterdam, two series of measurements were performed from 9 to 16 March 2011 and from 7 to 27 March 2013. Three monitoring locations were investigated in the first campaign: A-BG1, urban background, A-SM1, and A-SM2, all belonging to the Amsterdam Public Health Service (GGD), Dept. of Air Quality Monitoring Network. A-BG1 was located along the perimeter of an important city park, while A-SM1 and A-SM2 were street monitoring sites in the proximities of busy roads; anyway, the three sites lied in residential areas.

In 2011, $PM_{2.5}$ and $PM_{10}$ samples were collected daily at A-BG1, $PM_{2.5}$ at A-SM1 and $PM_{10}$ at A-SM2; samples were pooled to form composite weekly samples. In 2013, the above mentioned sites were investigated, but the whole period of monitoring was covered only at A-SM2. Two further

samples were collected at *A-BG2* on 23-24 March. The A-BG2 monitoring site was in a very quiet residential zone free from strong influence of traffic or other pollution sources. Samples were aggregated into weekday and weekend pools before laboratory analysis to increase the analyte amount while still allowing behavioural aspects to be examined.

In London, two campaigns were conducted, 7-27 March 2013 and 10-22 July 2014, aimed at determining the concentration levels of PS in the city, and the differences related to year and season (spring vs. summer). Daily $PM_{10}$ samples were collected at two stations belonging to London Air Quality Network, i.e. *L-BG*, urban background in a quiet residential area and *L-KS* (kerbside) close to a road frequently congested and hosting education buildings, tourist attractions, shops and housing in the surrounding area. In both campaigns the samples were aggregated on weekday and weekend basis before analysis.

In Stockholm, samples were taken at an urban background station in the city centre. The site is located on top of a building (ca. 20 m above the street) and can be regarded as representative of a large area of central Stockholm (Gidhagen et al., 2003; Johansson et al., 2009). The measurements were carried out between September and November, 2014. Daily $PM_{10}$ and $PM_{2.5}$ samples were collected and pooled into three groups, corresponding to 18 Sep - 1 Oct, 2-15 Oct and 30 Oct - 12 Nov.

The March 2011 campaign in Amsterdam was simultaneous to that carried out in the framework of the *Ariadrug* Project in Italy (Cecinato et al., 2012). The cities of Milan, Turin, Verona, Bologna, Florence, Rome, Naples and Palermo were investigated as representative of large and medium urban areas with different economic aptitudes, social contexts, and spread all over the Italian Peninsula. The March 2013 campaigns in Amsterdam and London were contemporary with that carried out in Rome (7-27 March) within a research activity dealing with pollution of interiors (Cecinato et al., 2014; Romagnoli et al., 2014). Four stations of ARPA Lazio Regional Network for Air Pollution Control were monitored in Rome, namely Cipro (CI) and Belloni (BE), residential, Francia (FR), street monitoring, and Villa Ada (VA), urban background inside the second largest green park in Rome.

Table 1 reports the sampling dates, size fraction sampled, and type of sites investigated in Amsterdam, London, Stockholm and Rome, together with data on population and population density of the cities.

*Table 1.*

### *2.2 Sampling and chemical analysis procedures*

Airborne particulate was collected daily onto PTFE or pure quartz fibre filters using medium volume samplers (38.3 L/min in Amsterdam and Rome, 16.7 L/min in London and Stockholm) equipped with size selective inlets. After collection, samples were sealed in clean holders, wrapped with aluminium foils and stored at low temperature prior to be analysed. Depending on the site, groups of 2 up to 14 individual particulate samples were assembled and processed as pools.

The method used for the analytical determination of licit and illicit drugs is an extension of the reference method EN 15549:2008, 'Air quality – Standard method for the measurement of concentration of benzo[a]pyrene in ambient air'. This aspect is very important when considering that cocaine could be easily determined in the frame of the routine activities imposed by the Air Quality Legislation for the monitoring of benzo(a)pyrene. An extensive description of the method applied is presented elsewhere (Cecinato et al., 2009, 2010). Briefly, the composite samples were spiked with deuterated standards and extracted through sonication using a dichloromethane:acetone mixture (4:1 in volume), reduced close to dryness under ultra-pure nitrogen and transferred onto a neutral alumina chromatographic column. Three fractions were collected by eluting with isooctane, isooctane-dichloromethane (3:2) and dichloromethane:acetone (1:1), in sequence. PAHs were in the second fraction while cocaine, nicotine, caffeine, THC, CBL and CBD were in the third (Cecinato et al., 2010).

After solvent evaporation and back dissolution into chloroform, the eluates containing PS were processed through GC-MSD (*Trace GC Ultra* coupled with *Trace DSQ*, both from Thermo Fisher, Rodano, Italy). Glass capillary chromatography was operated in temperature gradient (from 60°C to 280 °C) using a programmed-temperature vaporizer for injection (split-less time 1.25 min). A DBX type column (length = 25 m, i.d. = 0.20 mm, film thickness = 0.25 μm, purchased from Superchrom, Milan, Italy) to obtain the necessary separation of compounds was used. Mass spectrometric detection was operated in selected ion monitoring mode (SIM), using three ion current signals for each analyte and (minimum) two ion traces for the respective internal reference substance (Cecinato et al., 2012). The limits of detection (LODs) of cocaine and cannabinoids were of the order of 0.0003 μg/ml. The entire analytical features of the method was investigated by using the standard addiction method (SAM) (Gonzales and Herrador 2007) on real samples. For this purpose, portions of a homogeneous substrate of atmospheric particulate were fortified with different amount of analytes (three levels of concentrations plus blank, three replicates each level). The overall accuracy was calculated through the differences observed between the pure drug concentrations determined experimentally in the drug fortified samples and those added to them. The accuracy was quantified as 2.3±6.1% for cocaine. The precision was calculated by comparing the analyte concentrations detected in the samples and expressed as percent standard deviation; this

ranged between 4.7% and 6.9% for cocaine but was higher for cannabinoids. For this class, matrix effects and blanks contamination were observed by using SAM and a corresponding increase of uncertainty was observed (accuracy: 13-18%, precision 15-25%). Taking into account the performances of the analytical method and the necessary blank subtraction for cannabinoids the experimental limit of quantifications (LOQs) were defined. Samples analysed in this study were representative of different volumes of air collected. Considering the weekend samples of London, where ~ 55 $m^3$ of air were analysed (the lowest in this study) and the purified extracts were dissolved in 100 μL of solvent for analysis, the limits of quantifications of cocaine and cannabinoids were 0.003 ng/$m^3$ and 0.01 ng/$m^3$, respectively.

12 PAH compounds ranging from benz[a]anthracene (molecular mass = 228.2) up to dibenz[a,h]anthracene (molecular mass = 278.3) were characterized. Considering PAHs, caffeine and nicotine, the LOQs never exceeded 0.01 ng/$m^3$ and the overall accuracy was always better than 20%. Concentrations of $PM_{10}$ in Amsterdam, London and Rome were extracted from publicly available online databases (GGD Amsterdam 2016; London Air Quality Network, 2016; ARPALAZIO, 2016). The values of common meteorological variables (mean and maximum daily temperature, relative humidity, mean and maximum wind speed, precipitation occurrence) were also downloaded from free accessible web sites (Weather Underground, 2016) and are reported in Table S1.

### *2.3 Cocaine and cannabis abuse prevalence in the investigated countries*

According to the latest survey data provided by the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), in the United Kingdom and in Netherlands, drug abuse is widespread. In 2013 in the United Kingdom, the drugs abuse lifetime prevalences of cannabis and cocaine among adults (number of individuals that have experienced the abuse in the age range 15-64 y) were 29.9% and 9.5% respectively. In Netherland the last lifetime data, referring to 2009, report estimates equal to 25.7% and 5.2%, respectively, for the same substances. By contrast in Sweden the illicit drugs abuse looks less common and the lifetime prevalence recorded for cannabis is 14.4%, whereas the last year 15-34y prevalence is in the range 1.1-2%. (EMCDDA, 2015).

## 3. Results and discussion

### *3.1. Concentrations of PAHs, licit and illicit drugs in $PM_{10}$ and $PM_{2.5}$*

$PM_{10}$ was collected in London, while in Amsterdam and Stockholm the PM size fraction changed with the sampling periods and sites. Previous studies show that cocaine and cannabinoids are found in $PM_{2.5}$ with percentages never lower than 75% (Cecinato et al., 2010). To ensure a valid

comparison between countries it was first verified that $PM_{10}$ and $PM_{2.5}$ samples collected simultaneously and at the same site contained similar amounts of PAH and drug substances. Figure 1 illustrates the results for the $PM_{2.5}$ and $PM_{10}$ collected in Amsterdam at A-BG1, the percentages of individual PAH congeners in $PM_{2.5}$ compared to $PM_{10}$ were 89% ± 8%, and the percentages of drugs reached 102% ± 3%. A comparison was not made for cannabinoids due to the absence of these compounds in the samples. Cannabinol distribution was checked in Stockholm and its preponderance in $PM_{2.5}$ was confirmed.

Figure 1.

### *3.2. Psychotropic substances concentrations*

#### 3.2.1. *Amsterdam*

Due to the lack of preliminary information concerning the atmospheric concentrations of illicit drugs in Northern Europe, daily filters collected during March 2011 in Amsterdam were pooled to weekly samples in order to achieve LOQs for the analytical procedure. Table 2A shows the average values of the target compounds measured over the period. The A-BG1 urban background site was the least polluted for all classes. Considering regulated pollutants, small differences in the $PM_{10}$ levels were recorded among the sites (average 36±4 $\mu g/m^3$), by contrast, total PAHs showed larger variations. Total PAHs reached 1.13± 0.06 $ng/m^3$ at A-BG1, whereas they were 80% higher in A-SM1 (2.03 $ng/m^3$) and 50% higher in A-SM2 (1.68 $ng/m^3$). As for the psychotropic substances, caffeine ranged from 0.9 $ng/m^3$ at A-BG1 to 1.2 $ng/m^3$ at A-SM2. More marked differences among sites were observed for nicotine and cocaine. In particular, 0.03 $ng/m^3$ of cocaine and 6.7 ± 0.2 $ng/m^3$ of nicotine were valued at A-BG1 when at A-SM2 these compounds were over 4 times more (0.14 and 30.7 $ng/m^3$ respectively). Intermediate concentrations were measured at A-SM1. Cannabinoid concentrations were all below the quantification limit (< 0.01 $ng/m^3$ for each THC, CBL and CBD).

Table 2.

The concentrations measured in the 2013 campaign are reported in Table 2B. March was the coldest month of the 2013 in Amsterdam (see Table S1), with an average daily temperature of 0°C. This period was also characterized by the presence of rain and snow that could contribute to the decrease of atmospheric PM and nicotine recorded in 2013 compared with 2011. Meanwhile the PAH concentration increased, possibly due to the increased use of domestic heating (Alam et al., 2015).

Atmospheric cocaine variations were not consistent across the sites; a slight increase was observed at A-BG1 and A-SM1 and a drop at A-SM2. The maximum value of cocaine concentration detected in 2013 (0.12 ng/m$^3$) was recorded at A-SM2 (as it was in 2011) together with the peaks of nicotine (20.6 ng/m$^3$) and caffeine (9.1 ng/m$^3$) on 7-8 March. It is worth noting that A-SM2 site was close to a bus stop, and these peaks were probably related to variations in very local sources. Unlike 2011, cannabinol was quantifiable in almost all sites, except at A-BG2; this latter, confirming its feature of urban background, was the less affected by both PS and PAHs.

*3.2.2. London*

Table 3A/B reports the mean PS, PAH and $PM_{10}$ concentrations recorded at L-BG and L-KS during winter and summer seasons. Taking into account both seasons, the concentrations of PM, PAHs and nicotine were higher at L-KS. In particular, in March 2013 the maximum differences between sites were observed for nicotine. In this period at L-KS nicotine reached 27.5 ± 25.5 ng/m$^3$, almost twice the level detected at L-BG (14.3 ± 12.1 ng/m$^3$), even though the variability was large. Less important increases were observed for PAHs and $PM_{10}$. In July 2014 the biggest differences were found for PAHs (1.03 ± 0.24 ng/m$^3$ at L-KS compared to 0.67 ± 0.41 at L-BG), while nicotine and PM at L-KS exceeded 35- 40% of that measured at L-BG. The same behaviour was observed for caffeine that showed the highest mean concentrations at L-KS. This finding confirms that L-KS was, unsurprisingly, more influenced by traffic than L-BG, while the concentration of caffeine and nicotine could depend on peoples' activity in the area, due to its touristic and commercial attractions. By contrast, the maximum amounts of atmospheric cocaine were recorded at L-BG, with average values over the whole campaigns 3-4 times higher than those of L-KS.

The adverse weather conditions that affected the Northern Europe in March 2013 hit also London, with low average temperatures, rain and snow events which were expected to decrease the contaminants in the air. In this context, in London the highest value of cocaine concentration was detected again on 7-8 March (0.33 ng/m$^3$ at L-BG), and average cocaine concentration over the period reached 0.23 ± 0.11 ng/m$^3$ at L-BG and 0.05 ± 0.03 ng/m$^3$ at L-KS. In July, cocaine ranged between 0.18 ± 0.05 ng/m$^3$ at L-BG and 0.06 ± 0.01 ng/m$^3$ at L-KS. Rainy weather accompanied the July 2014 campaign, nonetheless almost all targeted compounds were, on average, more in March than in July. For cocaine, this finding confirms the results of the *Ariadrugs* project where measurements of illicit drugs were carried out weekly over one year. At all the eight cities investigated the lowest concentrations occurred in the summer period (June to August). This trend is not directly connected to any emission reduction, but relates to the increase of dispersion and of boundary layer height during the summer months. The only significant exception to this behaviour

is represented by cannabinol, the sole cannabinoid detected in London. This compound occurred at low but quantifiable concentrations in both seasons and sites (see Table 3). Comparing the sites, cannabinol at L-BG was of the same order of magnitude of that measured at L-KS. Comparing the seasons, the cannabinol behaviour in London was peculiar, because the highest concentration were recorded in July. According to the *Ariadrugs* Project results, in Italy cannabinoids dropped during the summer due to degradation effects induced by solar radiation (Carbone et al., 2010; Cecinato et al., 2012, 2016). The summer increase of atmospheric cannabinol measured in London probably depended on the increase or proximity of drug use.

Table 3.

### *3.2.3 Stockholm*

In Stockholm, due to the low concentrations expected for all chemicals, airborne particulates ($PM_{2.5}$ and $PM_{10}$) were gathered into three composite samples, corresponding to 18 Sep - 1 Oct, 2-15 Oct and 30 Oct - 12 Nov, 2014. The results are summarized in Table 4. Cocaine occurred only at detectable but not quantifiable levels. Cannabinol did not exceed 0.02 $ng/m^3$; meanwhile, the other contaminants occurred at lesser extents than in other cities.

Table 4.

### *3.3.Weekends vs. weekdays atmospheric concentrations*

Various attempts have been made to evaluate differences between weekdays and weekend concentrations of PSs in the atmosphere and to verify if they depended on the weekly trends in drug abuse rate, which are expected to be higher at the weekend. No clear difference was observed, probably due to the impact of atmospheric dispersion, however, the input of special events was detectable. For instance, an increase in cocaine concentration was observed in Rome during the celebration of the White Night Holidays in 2007, and a similar increase in cannabinoid concentrations was found in Barcelona during a massive street protest (Cecinato et al., 2009; Viana et al., 2010; Mastroianni et al., 2015).

Figure 2.

Figure 2 reports the weekend and weekday average concentrations of the investigated compounds (together with the associated variability over the period), measured in London during the sampling campaign carried out in March and July at L-BG (A and B) and L-KS (C and D).

With regard to cocaine, two distinct behaviours were observed. In March, the average concentration of cocaine on weekdays exceeded those measured on weekends both at L-BG and L-KS (though the differences were not statistically significant); the reverse behaviour was observed in July. To illustrate the influence of meteorology and local emission rate on the illegal drug ambient concentrations, the weekend vs. weekdays concentration ratio of cocaine was compared with those of PM and other pollutants (see Table 5).

Table 5.

During March 2013, all substances, except PAHs and caffeine at L-BG, decreased on weekends; the percent decrease of cocaine and PM were very similar at both sites, suggesting that atmospheric dispersion was an important driver of this trend. Thus, the increase of cocaine concentration during the weekdays cannot be associated to the increase of consumption. The reverse was observed in July at L-BG site. There, the cocaine and cannabinol concentrations were higher on weekends, despite the concurrent decrease of PM and other pollutants. In this case, the peculiar behaviour of cocaine could depend on the emission rate in the area, probably associated to consumption, rather than to an increase of population attending at the area. No marked differences were measured at L-KS in July between weekend and weekdays and between cocaine and other pollutants patterns.

In Amsterdam this approach was applicable only with regard to the March 2013 campaign. The particularly adverse meteorological conditions and the consequent strong influence of atmospheric mixing on the pollutant concentrations, combined with the shortness of data series available, hindered any clear observation of possible PS weekly trends. In fact, a widespread reduction in pollutant concentrations was recorded during weekends. The most important decrease was measured for caffeine at A-SM2 (weekend vs weekdays ratio equal to 0.1). This was possibly due to the different habits and number of people at the bus stop close to monitoring site.

### *3.4. Comparison of the contemporary monitoring campaigns*

A monitoring campaign was carried out in Rome from 7 to 27 March 2013, to compare the PS behaviour in the Northern and Southern Europe cities. Also in Rome the measurement period was

rainy and cold, which hindered the accumulation of atmospheric pollutants. Figure 3 illustrates the cocaine concentrations, site by site, in each city; the boxplots reported in the Supplementary Material (Figure S1) illustrate the distributions and principal statistical parameters of all concentrations detected in the cities (the A-BG2 sample in Amsterdam was not considered).

Figure 3.

Meteorology seems to regulate the general trend of the illicit drug concentrations, although this can be overwhelmed by strong local sources. Analogous conclusions were drawn by Mastroianni et al. (2015) studying 12 sites simultaneously monitored in Barcelona. Comparing the average concentrations measured over the period in London, Amsterdam and Rome, London was the most contaminated city with regards to cocaine, in agreement with the highest levels of abuse associated to the UK (EMCDDA, 2015).

The average cocaine concentration calculated over the whole period at both London sites was equal to 0.15±0.11 ng/m$^3$. Slightly higher levels of consumptions are estimated for the Netherlands compared to Italy, however in Amsterdam the mean concentration of cocaine was lower than in Rome, 0.06±0.03 ng/m$^3$ vs. 0.09±0.03.ng/m$^3$. This finding probably depended on the higher population in Rome and the small scale house density at the sites investigated (two or three times higher than the average all over the city for Belloni, Cipro and Francia). This hypothesis is confirmed by the fact that, although the Spanish prevalence of consumption is comparable to that of UK, the average amount of cocaine detected by Mastroianni in the densely populated Barcelona was equal to 0.27 ng/m$^3$. Barcelona population and population density reach 1,600,000 units and 15,700 inhabitants/km$^2$, respectively. Another opportunity to compare contemporary data of illicit atmospheric drugs in Northern and Southern Europe was offered by data collected in Amsterdam and eight Italian cities in March 2011. Table 6 reports the cocaine and cannabinoids levels detected in Italy and the features of the sites. Mean cocaine concentration in Amsterdam during 2011 reached 0.07± 0.03 ng/m$^3$ and was similar to amounts detected at the urban background site of Milan (Pascal station, located in a public garden) and at the traffic site of Florence, lying in a densely populated city district. Concerning cannabinoids, in Italy only cannabinol was detected in Turin and Palermo, whereas in the other cities most of the investigated cannabinoids occurred at levels above LOQ. Rome showed the highest level of the cannabis active principle THC. Contemporarily cannabinoids were not detected in Amsterdam and, as reported in the text, their concentrations in Northern Europe were in general lower than in Italy even though the consumption

is more widespread there. Our hypothesis is that cannabinoids were consumed more indoors in Northern Europe, or that air ventilation of buildings favoured in Italy resulted in greater emissions.

Table 6.

*3.5. Comparison of atmospheric cocaine concentrations with wastewater analysis*

Estimates of consumption rates are principally acquired using statistics of crimes or phenomenon related to drugs abuse and population surveys. Relevant uncertainty exists on data produced on this basis due to the difficulties in the acquisition of correct information, as a consequence results produced by different areas are scarcely comparable. However, these tools are very expensive, time consuming and unsuitable for the rapid identification of drug prevalence variations. Illicit substances and their metabolites are excreted by consumers in known percentages, and the characterization of residues in wastewater is currently accepted as a new suitable tool to assess the drug consumption, appearing as a direct and relatively cost effective "measurement" of drug abuse (EMCDDA 2016a).

Though the per capita drug consumption is not deliverable from concentrations in air, the cocaine method used here is a simple extension of procedures adopted for measuring particulate bound PAHs at the regional Air Quality Monitoring networks, and a possible cost-effective tool to index the impact of phenomenon on the territory. In fact cocaine is stable in the atmosphere, and its atmospheric concentration looks less affected than cannabinoids by consumption habits. In this perspective, the comparison with results of measurement performed in wastewater (the sole quantitative method to obtain per capita drug consumption estimates) is crucial to verify whether this is achievable. The present study, together with previous investigations, allowed us to combine the data sets of atmospheric concentrations for the first time at a European level, to correlate atmospheric concentrations of cocaine with the abuse estimates obtained by wastewater analysis for the same year (See Figure 4). When available (2012 and 2013), data were taken from the EMCDDA database (EMCDDA 2016b), otherwise they were collected from literature (Thomas et al., 2011; Zuccato and Castiglioni, 2012; DPA, 2012). Cocaine abuse estimates for Stockholm in 2014 were not available, therefore the wastewater data refer to 2013 (Ort et al., 2014).

Figure 4.

Taking in account all Italian cities, London, Stockholm and Amsterdam in 2013, a good level of correlation was found between the atmospheric concentration of cocaine and the amount of the residues in wastewater ($R^2$= 0.66; p = 0.00131). The $R^2$ value was improved (0.88; p = $1.9828*10^{-5}$) by omitting Turin, where the atmospheric monthly concentration was generated by analysing five daily samples, which reduced the sample representativeness. Poor correlation ($R^2$= 0.22) is obtained by inserting data from Barcelona and Amsterdam 2011. The large differences in the results of wastewater analysis recorded for Amsterdam in 2011 and 2013 do not correspond to the range of variation observed for cocaine in the atmosphere. On the other hand the large amount of cocaine in the air of Barcelona does not fit with daily consumption estimate produced by wastewater analysis for the same year, perhaps due to the high population density in the city.

These findings highlight further limitations of atmospheric measurements to assess the drugs prevalence in the community (in addition to meteorology), that a at much minor extent also belong to the wastewater analysis tool. These are principally due to the large fluctuations in abuse over time, which requires consistent time coverage of the data collected to be mediated, and to the need of an additional tool able to account for local population. (van Nuijs et al., 2011).

The population data is required to normalize the absolute values of illicit substances affecting the atmosphere and wastewater. In this regard, the number of residents is a useful but incomplete parameter because population can widely exceed the resident population due to the daily influx of commuters and visitors, especially in the big cities. Therefore, attempts to define normalization factors are important for both approaches (Cecinato et al., 2013; Bruno et al., 2014).

## Conclusions

This study reports the first European data series of ambient psychotropic substances with the respective geographical and temporal variations, and compares them with the outcomes of wastewater analysis method for assessing population drug consumption. Ambient measurements in Amsterdam, Stockholm and London confirmed the presence of both licit (nicotine, caffeine) and illicit drugs (cocaine, cannabinoids) in the atmosphere and the corresponding concentrations rates were compared with measurements performed in Italian cities. The concentration of PSs were found to vary with both city location and season, which provided the opportunity to investigate geographical and temporal variations in some detail. Among cannabinoids, only cannabinol was detected in the Northern Europe cities. In Amsterdam and London, the cannabis prevalence is reported as higher than in Italy, whilst concentration in air was not. This is likely the result of consumer behavior. Further studies are necessary to clarify this issue but the rate of indoor drug consumption, or the average amount per dose could play a key role. The highest concentrations of

475 cocaine were recorded in London, where the background site investigated was unexpectedly more
476 affected by cocaine than the city centre location. In Stockholm cocaine was not detected in
477 quantifiable amounts (>3 pg/$m^3$). The average concentration detected in March 2011 in Amsterdam
478 was similar to that contemporarily detected in a densely populated area in Florence and in a
479 background site in Milan. A measurement campaign carried out in London, Amsterdam and Rome
480 in March 2013 showed that meteorology was the principal driver of atmospheric cocaine
481 concentrations, but that the inputs of local sources were very relevant. A clear observation of
482 weekly consumption modulation through ambient concentration of illicit drugs was masked by the
483 effect of variations in atmospheric dispersion. This phenomenon could not be controlled for in these
484 short studies, however an attempt was made through comparing the drug concentrations with those
485 of other pollutants. This allowed us to detect a clear weekend-weekday cocaine modulation in July,
486 at one site in London. Further studies are necessary to better understand how meteorology and
487 consumption behavior relate to ambient concentrations of PSs. Nevertheless measuring atmospheric
488 drug concentrations provides a feasible method to capture the differences in drugs consumption
489 between areas and over time. The suitability of this approach to become a tool to index the impact
490 of drug abuse (e.g. cocaine) was investigated by comparing the results of this study to those of the
491 wastewater analysis, routinely used to estimates the consumption prevalence. A good correlation
492 was found when the temporal variability of the consumption and the population were accounted for.
493 Atmospheric measurements of PSs could therefore offer a useful complementary approach to
494 wastewater analysis of PSs, especially where local hot spots need to be identified.

495 References

496 Alam, M.S., Keyte, I.J., Yin J., Stark, C., Jones, A.M., Harrison, R.M., 2015. Diurnal variability of
497 polycyclic aromatic compound (PAC) concentrations: Relationship with meteorological conditions
498 and inferred sources. Atmos. Environ. 122, 427-428.
499
500 Álvarez-Ruiz, R., Andrés-Costa, M.J., Andreu, V., Picó, Y., 2015. Simultaneous determination of
501 traditional and emerging illicit drugs in sediments, sludges and particulate matter. J. Chromatogr. A
502 1405, 103–115.

503 ARPALAZIO, Agenzia Regionale Protezione ambientale del Lazio, 2016,
504 http://www.arpalazio.gov.it/ambiente/aria. (last accessed 09/09/2016).

505 Balducci, C., Nervegna, G., Cecinato, A., 2009. Evaluation of principal cannabinoids in airborne
506 particulates. Anal. Chim. Acta 641, 89–94.

507 Bianchi, F., Bisceglie, F., Dugheri, S., Arcangeli, G., Cupelli, V., del Borrello, E., Sidisky, L.,
508 Careri, M., 2014. Ionic liquid-based solid phase microextraction necklaces for the environmental
509 monitoring of ketamine. J. Chromatogr. A 1331, 1-9.

510 Bruno, R., Hall, W., Kirkbride, P., Yin Lai, F., O'Brien, W., Prichards, J., Thai, P.K., Mueller, J.F.,
511 2014. Commentary on Ort *et al*. (2014):What next to deliver on the promise of large scale sewage-
512 based drug epidemiology? *Addiction* 109, 1353–1354.

513 Carbone, M., Castelluccio, F., Daniele, A., Sutton, A., Ligresti, A., Di Marzo, V., et al., 2010.
514 Chemical characterisation of oxidative degradation products of $\Delta^9$-THC. Tetrahedron 66, 9497-
515 9501.

516 Castiglioni, S., Thomas, K.V., Kasprzyk-Hordern, B., Vandam, L., Griffiths, P., 2014. Testing
517 wastewater to detect illicit drugs: State of the art, potential and research needs. Sci. Total Environ.
518 487, 613–620.

519 Cecinato, A., Balducci, C., 2007. Detection of cocaine in the airborne particles of the Italian cities
520 Rome and Taranto. J. Sep. Sci. 30, 1930–1935.

521 Cecinato, A., Balducci, C., Nervegna, G., 2009. Occurrence of cocaine in the air of the World's
522 cities. An emerging problem? A new tool to investigate the social incidence of drugs? Sci. Total
523 Environ. 407, 1683-1690.

524 Cecinato, A., Balducci, C., Budetta, V., Pasini, A., 2010. Illicit psychotropic substance contents in
525 the air of Italy. Atmos. Environ. 44, 2358-2363.

526 Cecinato, A., Balducci, C., Romagnoli, P., Perilli, M., 2012. Airborne psychotropic substances in
527 eight Italian big cities: Burdens and behaviours. Environ. Pollut. 171, 140-147.

528 Cecinato, A., Balducci, C., Mollica, R., Serpelloni, G., 2013. Social [and health] relevance of
529 psychotropic substances monitoring in air. Environ. Pollut. 179, 27-32.

530 Cecinato, A., Balducci, C., Romagnoli, P., Perilli, M., 2014. Behaviours of psychotropic substances
531 in indoor and outdoor environments of Rome, Italy. Environ. Sci. Pollut. Res. 21, 9193–9200.

532 Cecinato, A., Balducci, C., Perilli, M., 2016. Illicit psychotropic substances in the air: the state-of-
533 art. Sci. Total Environ. 539, 1-6.

534 Daughton, C.G., 2011. Illicit drugs: contaminants in the environment and utility in forensic
535 epidemiology. Rev. Environ. Contam. Toxicol. 210, 59-110.

536 De Giorgio, F., Strano Rossi, S., Rainio, J., Chiarotti, M., 2004. Cocaine found in a child's hair due
537 to environmental exposure?. Int. J. Legal Med. 118, 310-312.

538 DPA. Department for Anti-drug Policies of the Presidency of Ministers' Council of Italy, 2012.
539 Annual Report to Parliament. Available from:
540 http://www.politicheantidroga.gov.it/attivita/pubblicazioni/relazioni-al-parlamento/relazione-
541 annuale-2012/presentazione.aspx (last accessed 09/09/2016).

542 European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), 2015. European Drug
543 Report, trends and developments. Luxembourg: Publications Office of the European Union.
544 http://www.emcdda.europa.eu./publications/edr/trends-developments/2015 (last accessed
545 09/09/2016).

546 European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), 2016a. Assessing illicit
547 drugs in wastewater: advances in wastewater-based drug epidemiology, Insights 22, Publications
548 Office of the European Union, Luxembourg. ISBN 978-92-9168-856-2.

549 European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), 2016b. Wastewater
550 analysis and drugs - a European multi-city study. http://www.emcdda.europa.eu/topics/pods/waste-
551 water-analysis. (last accessed 09/09/2016).

552 Garcia-Bournissen, F., Nesterenko, M., Karaskov, T., Koren, G. 2009. Passive environmental
553 exposure to cocaine in Canadian children. Pediatr. Drug. 11, 30-32.Gidhagen, L., Johansson, C.,
554 Ström, J., Kristensson, A., Swietlicki, E., and Pirjola, L., 2003. Model simulation of ultrafine
555 particles inside a road tunnel. Atmospheric Environment, 37, 2023-2036.

556 Gonzales, A.G., Herrador, M.A., 2007. A practical guide to analytical method validation, including
557 measurement uncertainty and accuracy profiles. Trends Anal. Chem. 26, 227–38.

558 Hannigan, M.P., Cass, G.R., Penman, B.W., Crespi, C.L., Lafleur, A.L., Busby Jr., W.F., et al.,
559 1998. Bioassay-directed chemical analysis of Los Angeles airborne particulate matter using a
560 human cell mutagenicity assay. Environ. Sci. Technol. 32, 3502–3514.

561 Hu, D., Chen, J., Ye, X., Li, L., Yang, X., 2011. Hygroscopicity and evaporation of ammonium
562 chloride and ammonium nitrate: Relative humidity and size effects on the growth factor.
563 Atmospheric Environment 45, 2349-2355.

564 Huerta-Fontela, M., Galceran, M.T., Ventura, F., 2008. Stimulatory drugs of abuse in surface waters
565 and their removal in a conventional drinking water treatment plant. Environ. Sci. Technol. 42,
566 6809-6816.

567 Johansson, C., Burman, L., Forsberg, B. 2009. The effects of congestions tax on air quality and
568 health. Atmos. Environ. 43, 4843-4854.

569 Kelly, J.T., Baker, K.R., Nolte, C.G., Napelenok, S.L., Keene, W.C., Pszenny, A.A.P., 2016.
570 Simulating the phase partitioning of NH3, HNO3, and HCl with size-resolved particles over
571 northern Colorado in winter. Atmospheric Environment 131, 67-77.

572 Kidwell, D.A., Blanco, M.A., Smith, F.P., 1997 Cocaine detection in a university population by hair
573 analysis and skin swab testing. Forensic Sci. Int. 84, 75-86.

574 Ladji, R., Yassaa, N., Balducci, C., Cecinato, A., Meklati, B.Y., 2009 Annual variation of
575 particulate organic compounds in PM10 in the urban atmosphere of Algiers. Atmos. Res. 9, 258-
576 269.

577 London Air Quality Network, 2016. www.londonair.org.uk. ( last accessed 09/09/2016).

578 Mastroianni, N., Postigo, C., De Alda, M.L., Barcelo, D., 2013. Illicit and abused drugs in sewage
579 sludge: Method optimization and occurrence. J. Chromatogr. A. 1332, 29-37.

580 Mastroianni, N., Postigo, C., De Alda, M. L., Viana, M., Rodríguez, A., Alastuey, A., Querol, X.,
581 Barceló, D., 2015. Comprehensive monitoring of the occurrence of 22 drugs of abuse and
582 transformation products in airborne particulate matter in the city of Barcelona. Sci. Total Environ.
583 532, 344–352.

584 McKenzie, E. J., , Miskelly, G.M., Butler, P. A. G., 2013. Detection of methamphetamine in
585 indoor air using dynamic solid phase microextraction: a supplementary method to surface wipe
586 sampling. Anal. Method. 5, 5418- 5424.

587 Moussaoui, Y.,Balducci, C., Cecinato, A., Meklati, B.Y., 2013. Atmospheric particulate organic
588 matter at urbanand forest sites of Northern Algeria. Urban Clim. 4, 85-101.

589 Ort, C., van Nuijs, A. L. N., Berset, J.D., Bijlsma, L., Castiglioni, S., Covaci A., de Voogt, P, et al.,
590 2014. Spatial differences and temporal changes in illicit drug use in Europe quantified by
591 wastewater analysis. Addiction 109, 1338–1352.

592 Perrino, C., Pietrodangelo, A., Febo, A., 2001. An atmospheric stability index based on radon
593 progeny measurements for the evaluation of primary urban pollution. Atmos. Environ. 35,5235–
594 5344.

595 Pichini, S., Garcia-Algar, O., Alvarez, A., Gottardi M., Marchei, E., Svaizer F., Pellegrini, M.,
596 Rotolo, M.C., Pacifici, R., 2014. Assessment of unsuspected exposure to drugs of abuse in children
597 from a Mediterranean City by hair testing. Int. J. Environ. Res. Public Health. 11, 2288–2298.

598 Postigo, C., Lopez de Alda, M.J., Viana, M., Querol, X., Alastuey, A., et al., 2009. Determination
599 of drugs of abuse in airborne particles by pressurized liquid extraction and liquid chromatography-
600 electrospray-tandem mass spectrometry. Anal. Chem. 81, 4382–4388.

601 Romagnoli, P., Balducci, C., Perilli, M., Gherardi, M., Gordiani, A., et al. Indoor PAHs at schools,
602 homes and offices in Rome, Italy. Atmos. Environ. 92, 51-59, 2014.

603 Seabra Pereira, C.D., Luciane, A., Maranho, L.A., Cortez, F.S. , Pusceddu, F.H., Santos, A.R.,
604 Ribeiro, et al.,. 2016. Occurrence of pharmaceuticals and cocaine in a Brazilian coastal zone. Sci.
605 Total Environ. 548–549, 148–154.

606 GGD Amsterdam, Air Quality Monitoring Network, https://www.luchtmeetnet.nl. (last accessed
607 09/09/2016).

608 Thomas, K. V., Bijlsma, L., Castiglioni, S., Covaci, A., Emke, E., Grabic, R., Hernández, F., et al.,
609 2012. Comparing illicit drugs use in 19 European cities through sewage analysis. Sci. Total
610 Environ. 432, 432–439.

611 van der Aa, M., Bijlsma, L., Emke E. , Dijkman E. , van Nuijs A.L.N., van de Ven B. , Hernández
612 F. , et al., 2013. Risk assessment for drugs of abuse in the Dutch watercycle. Water Res. 47, 1848-
613 1857.

614 van Nuijs, A.L.N., Castiglioni, S.,Tarcomnicu, I., Postigo, C., Lopez de Alda, M., Neels, H., et al.,
615 2011. Illicit drug consumption estimations derived from wastewater analysis: A critical review. Sci.
616 Total Environ. 409, 3564–3577.

617 Viana, M., Querol, X., Alastuey, A., Postigo, C., López de Alda, M.J., et al., 2010. Drugs of abuse
618 in airborne particulates in urban environments. Environ. Internat. 36, 527–534.

619 Viana, M., Postigo, C., Querol, X., Alastuey, A., Lopez de Alda, M.J., et al., 2011. Cocaine and
620 other illicit drugs in airborne particulates in urban environments: A reflection of social conduct and
621 population size. Environ. Pollut. 159, 1241-1247.

622 Weather Underground 2016. https://www.wunderground.com/history/ (last accessed 09/09/2016)

623 Zuccato, E., Castiglioni S., 2012. Consumi di sostanze stupefacenti nelle città europee
624 Ricerca&Pratica 28, 252-260.

625 Zuccato, E., Chiabrando, C., Castiglioni, S., Calamari, D., Bagnati R., Schiarea, S., Fanelli, R.,
626 2005. Cocaine in surface waters: a new evidence-based tool to monitor community drug abuse.
627 Environ. Health Perspect. 5, 14.
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629

630 **Table headings**

631

632 Table 1. Population rate and density of the cities investigated. PM fraction sampled, sampling dates
633 and typology of the monitoring sites in each city.
634 Symbols adopted for sites: BG = urban background; KS= kerbside; SM= street monitoring.

635

636 Table 2. Average concentrations of nicotine (NIC), caffeine (CAF), cocaine (COC), polycyclic
637 aromatic hydrocarbons (PAH), $PM_{10}$ and cannabinol (CBL) in the atmosphere of Amsterdam. A) 9-
638 16 March 2011; B) 7-27 March 2013. na: not available.
639 $^{(*)}$ Sampling limited to 23– 24 March.

640

641 Table 3. Average concentrations of nicotine, caffeine, cocaine, cannabinol, polycyclic aromatic
642 hydrocarbons and $PM_{10}$ in the atmosphere of London A) 7-27 March 2013; B) 10-22 July 2014.
643 For compound symbols see Table 2

644

645 Table 4. Average concentrations of nicotine, caffeine, cocaine, cannabinol and polycyclic aromatic
646 hydrocarbons in the atmosphere of Stockholm. For compound symbols see Table 2

647

648 Table 5. Ratios of weekend vs. weekdays pollutants concentrations recorded in London in March
649 2013 and July 2014 and in Amsterdam in March 2013.

650

651 Table 6. Concentrations of cocaine (COC), cannabinol (CBL), $\Delta^9$-tetrahydrocannabinol (THC) and
652 cannabidiol (CBL) detected in 8 Italian cities in March 2011. Population, population density and
653 sites typology. TR= traffic site, BG= urban background.

654

655 Table S1. Mean values of average ($T_{ave}$) and maximum ($T_{max}$) daily temperature, relative humidity
656 (RH), barometric pressure (P), precipitation days (%), maximum ($w_{max}$) and minimum ($w_{min}$) daily
657 wind speed, and prevailing wind direction ($w_{dir}$) in London, Amsterdam and Rome. 7-27 March,
658 2013.

659

660 **Figure captions**

661

662 Figure 1. $PM_{2.5}/PM_{10}$ concentration ratio of polycyclic aromatic hydrocarbons and psychotropic
663 substances. Amsterdam, A-BG1 station, 9-16 March 2011.
664 Symbols: BaA = benz[a]anthracene; BbF = benzo[b]fluoranthene; BjF = benzo[j]fluoranthene; BkF
665 = benzo[k]fluoranthene; BaP = benzo[a]pyrene; IP = indeno[1,2,3-cd]pyrene; DBA = dibenz[a,h]
666 anthracene; BPE = benzo[ghi]perylene; NIC = nicotine; CAF = caffeine; COC = cocaine.

667

668 Figure 2. Weekends and weekdays average concentrations valuated in March and July at L-BG (A
669 and B) and L-KS (C and D) and associated variability of the concentrations over the periods. $PM_{10}$
670 are given in $\mu g/m^3$ units, all other chemicals in $ng/m^3$.
671 Symbols: NIC = nicotine; CAF = caffeine; COC = cocaine; CBL = cannabinol.

672

673 Figure 3. Cocaine concentrations detected in London, Amsterdam and Rome. Sampling period 7-27
674 March 2013.

675

676 Figure 4. Average aerial concentration of cocaine in European cities and estimates of the drugs
677 abuse produced by wastewater analysis in the same year.

678

679 Figure S1. Box plots reporting values of cocaine concentrations recorded in London, Amsterdam
680 and Rome in March 2013. Box boundaries represents 25 and 75 percentiles, the average is indicated
681 with the dotted line, median with continuous line. Whiskers represent minimum and maximum.

# Cocaine and cannabinoids in the atmosphere of Northern Europe cities, comparison with Southern Europe and wastewater analysis

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**Keywords: Illicit drugs; cocaine; atmosphere, $PM_{10}$; wastewater analysis.**

## Abstract

This study reports the first investigation of atmospheric illicit drug concentrations in Northern Europe using measurements of cocaine and cannabinoids in Amsterdam, London and Stockholm. Further, these measurements were compared to those made in Rome to explore the geographical and inter-city variability. Co-located measurements of atmospheric particulate mass and PAHs were used to help describe and interpret the illicit drug measurements with respect to atmospheric dispersion. Cocaine concentrations ranged from 0.03 to 0.14 ng/m$^3$ in Amsterdam, from 0.02 to 0.33 ng/m$^3$ in London and were below quantification limit (3 pg/m$^3$) in Stockholm. Cannabinol was the only cannabinoid molecule detected in the three cities. During this campaign, London reported the highest concentrations of cocaine and meaningful differences were detected between the urban background and city centre London sites. Mean cocaine concentrations measured in Amsterdam during March 2011 were also compared with those measured simultaneously in eight Italian cities. The cocaine concentration in Amsterdam was comparable to that measured at an urban background in Milan and at a densely populated site in Florence. Although correlating atmospheric

concentrations directly with drug prevalence is not possible using current data, links between concentrations of cocaine and estimates of abuse prevalence assessed by the more routinely used wastewater analysis were also examined. A statistically significant correlation was found between the two sets of data ($R^2$= 0.66; p = 0.00131). Results confirmed that meteorology, population rate and habits of consumption influence the atmospheric concentrations of drugs. If these confounding factors were better controlled for, the techniques described here could became an easy and cost effective tool to index the impact of cocaine abuse in the area; especially where local hot spots need to be identified.

## 1. Introduction

In recent years, environmental research has gained an increasing interest in new classes of compounds, comprising illicit psychotropic substances (PS). Although the potency of the biological effects of illicit drugs is recognized, very little is known about their potential harmful impact on the environment (Daughton, 2011). Most investigations have focused on developing tools to evaluate the abuse prevalence by measuring levels of drug residuals in wastewater (Zuccato et al., 2005; Thomas et al., 2012; Mastroianni et al., 2013; Ort et al., 2014; Castiglione et al. 2014 ). Traces of illicit substances have also been found worldwide in surface and drinking waters (Seabra Pereira et al., 2016; van der Aa et al., 2013; Huerta-Fontela et al., 2008) and in sediments and sludges (Álvarez-Ruiz et al., 2015). In this context the ambient atmospheric concentrations have been less well studied despite evidence of cocaine presence in the atmospheric particulate being reported since 1998 (Hannigan et al., 1998). Acute health risk associated with exposure to typical ambient concentrations of illicit drugs has been regarded as negligible (Viana et al., 2010). Nonetheless, the occurrence of illicit drugs in the air merits concern, taking into account that the atmosphere is a key pathway of dispersion both at local and global scale, and the risks posed by chronic exposure to these substances are completely unknown (Mastroianni et al., 2015). This issue is even more important when considering that dedicated investigations have reported that indoor air (houses, offices, primary schools and shops) can be more contaminated by illicit drugs than ambient air (Cecinato et al. 2014, 2016; Bianchi et al., 2014) even where drugs are not consumed. To date little information exists at this regard (McKenzie et al. 2013), but this phenomenon is expected to be accentuated at locations close to drug abuse or manufacture. In fact, cases of positive response to bioassays have been reported both in children and adults even in the absence of direct drug consumption (Kidwell et al. 1997; De Giorgio et al. 2004; Garcia-Bournissen et al 2009; Pichini et al. 2014). In ambient air the highest concentrations of these substances have been reported from spot measurements carried out in Latin America. Cocaine concentrations as high as 17 ng/$m^3$ were

found in Mexico City, and 3.3 ng/m$^3$ in Santiago De Chile (Cecinato et al. 2016). Cocaine was not found in Algeria, both in Algiers and surrounding areas (Ladji et al. 2009; Moussaoui et al. 2013), while traces of cannabinoids were detected. In Europe, some measurements have been made in Oporto, Portugal, and Pančevo, Serbia, but most have been made in Italy and Spain (Cecinato et al., 2009, 2010, 2012; Postigo et al., 2009; Viana et al., 2010, 2011; Mastroianni et al., 2015). In Italy, a number of localities have been investigated for cocaine and three important cannabinoids, i.e. $\Delta^9$-tetrahydrocannabinol (THC), cannabinol (CBL) and cannabidiol (CBD) (Balducci et al., 2009). In Spain, only three cities have been investigated, but a wider range of substances were studied, including native species, by-products and metabolites (e.g., amphetamines, heroin, cocaethylene, ecstasy, benzoylecgonine, 6-acetylmorphine). This study reports the first atmospheric measurements of cocaine and cannabinoids carried out in London, Stockholm and Amsterdam. Wide differences in meteorological and social contexts, as well as in the drug abuse prevalence, characterize the northern European cities studied; differences also exist between them and the southern European cities so far investigated. From this perspective, the first aim of this study is to provide new information on the variability of the ambient concentration of illicit drugs which reflect the differences between these cities. The second aim is to investigate the possible associations between the atmospheric concentrations and the abuse rate in the area detected there.

The concentration of illicit drugs in the atmosphere is controlled by meteorological dispersion, and little is known about drug suspension and transport from sources to the measurement locations. Using ambient concentration measurements of illicit drugs for consumption estimates is therefore unreliable using the current, limited datasets and significant challenges exist to control for variability in atmospheric dispersion. Nonetheless, studies conducted so far provide evidence that this approach can capture differences among geographical localities, locations or zones within a given area, as well as time variations from a few days to consecutive years (Cecinato et.al., 2014). Therefore, measuring illicit drug concentrations in the air could potentially be applied as a new tool to identify local hot spots, which can be associated with consumption, trafficking and manufacture of substances. Recent studies suggest cocaine may be feasible for this purpose. In fact, cocaine is overall associated to the particulate phase (Cecinato and Balducci 2007) and its determination in the PM accounts for total amount in the air. Although no specific studies have been carried out to assess the stability of illicit drugs in the atmosphere, the relative stability of cocaine seems to be inferred by its seasonal behavior, which looks analogous to that of the PM (Perrino et al. 2001; Hu et al., 2011; Kelly et al., 2016), and the winter/summer concentration ratios for cocaine and $PM_{2.5}$ were broadly similar. For instance, in Rome, taking in account 11 sites, ratios as high as 2.1 ± 1.2 and 2.5 ± 0.9, respectively, were observed for cocaine and $PM_{2.5}$. On the contrary cannabinoids (the other

extensively investigated class) have been shown to be markedly less stable showing a reduction of concentration (Cecinato et al., 2012, 2014).

The determination of cocaine and cannabinoids in the atmosphere of Northern Europe cities allowed us to further investigate links between ambient concentration and the drug addiction phenomenon. Accepting that the current knowledge is not advanced enough to quantify usage rates using ambient samples, these measurements may allow an indexing system of illicit drug prevalence to be developed using the existing sampling infrastructure available in all cities. To investigate this, atmospheric illicit drug concentrations were compared between London, Amsterdam and Rome in March 2013 as well as concentrations measured in Amsterdam and eight Italian cities in 2011. This allowed the influence of meteorology and population habits on the illicit drug concentrations to be examined.

The psychotropic compounds nicotine (NIC) and caffeine (CAF) (reported in the text as licit drugs) and polycyclic aromatic hydrocarbons (PAH) were monitored in addition, to provide insights into the characteristics of the sites and eventual peculiarities in the behaviour of illicit drugs (cocaine and cannabinoids). The improvement of the existing illicit drug concentration database, obtained through this study, allowed an examination of the concentrations of atmospheric cocaine over Northern and Southern Europe cities in the light of the drug prevalence in the respective countries. Measurements were also compared to estimates of collective consumption obtained through analysis of drug residuals in wastewater. The effectiveness of this methodology in assessing drug abuse prevalence is ascertained, and the comparison between the outcomes of the two types of study provides important information to verify if the illicit drugs impact over a certain area can be indexed through measurements in the air.

## 2. Experimental

### *2.1. Sites and periods of sampling*

In Amsterdam, two series of measurements were performed from 9 to 16 March 2011 and from 7 to 27 March 2013. Three monitoring locations were investigated in the first campaign: A-BG1, urban background, A-SM1, and A-SM2, all belonging to the Amsterdam Public Health Service (GGD), Dept. of Air Quality Monitoring Network. A-BG1 was located along the perimeter of an important city park, while A-SM1 and A-SM2 were street monitoring sites in the proximities of busy roads; anyway, the three sites lied in residential areas.

In 2011, $PM_{2.5}$ and $PM_{10}$ samples were collected daily at A-BG1, $PM_{2.5}$ at A-SM1 and $PM_{10}$ at A-SM2; samples were pooled to form composite weekly samples. In 2013, the above mentioned sites were investigated, but the whole period of monitoring was covered only at A-SM2. Two further

samples were collected at *A-BG2* on 23-24 March. The A-BG2 monitoring site was in a very quiet residential zone free from strong influence of traffic or other pollution sources. Samples were aggregated into weekday and weekend pools before laboratory analysis to increase the analyte amount while still allowing behavioural aspects to be examined.

In London, two campaigns were conducted, 7-27 March 2013 and 10-22 July 2014, aimed at determining the concentration levels of PS in the city, and the differences related to year and season (spring vs. summer). Daily $PM_{10}$ samples were collected at two stations belonging to London Air Quality Network, i.e. *L-BG*, urban background in a quiet residential area and *L-KS* (kerbside) close to a road frequently congested and hosting education buildings, tourist attractions, shops and housing in the surrounding area. In both campaigns the samples were aggregated on weekday and weekend basis before analysis.

In Stockholm, samples were taken at an urban background station in the city centre. The site is located on top of a building (ca. 20 m above the street) and can be regarded as representative of a large area of central Stockholm (Gidhagen et al., 2003; Johansson et al., 2009). The measurements were carried out between September and November, 2014. Daily $PM_{10}$ and $PM_{2.5}$ samples were collected and pooled into three groups, corresponding to 18 Sep - 1 Oct, 2-15 Oct and 30 Oct - 12 Nov.

The March 2011 campaign in Amsterdam was simultaneous to that carried out in the framework of the *Ariadrug* Project in Italy (Cecinato et al., 2012). The cities of Milan, Turin, Verona, Bologna, Florence, Rome, Naples and Palermo were investigated as representative of large and medium urban areas with different economic aptitudes, social contexts, and spread all over the Italian Peninsula. The March 2013 campaigns in Amsterdam and London were contemporary with that carried out in Rome (7-27 March) within a research activity dealing with pollution of interiors (Cecinato et al., 2014; Romagnoli et al., 2014). Four stations of ARPA Lazio Regional Network for Air Pollution Control were monitored in Rome, namely Cipro (CI) and Belloni (BE), residential, Francia (FR), street monitoring, and Villa Ada (VA), urban background inside the second largest green park in Rome.

Table 1 reports the sampling dates, size fraction sampled, and type of sites investigated in Amsterdam, London, Stockholm and Rome, together with data on population and population density of the cities.

*Table 1.*

### *2.2 Sampling and chemical analysis procedures*

Airborne particulate was collected daily onto PTFE or pure quartz fibre filters using medium volume samplers (38.3 L/min in Amsterdam and Rome, 16.7 L/min in London and Stockholm) equipped with size selective inlets. After collection, samples were sealed in clean holders, wrapped with aluminium foils and stored at low temperature prior to be analysed. Depending on the site, groups of 2 up to 14 individual particulate samples were assembled and processed as pools.

The method used for the analytical determination of licit and illicit drugs is an extension of the reference method EN 15549:2008, 'Air quality – Standard method for the measurement of concentration of benzo[a]pyrene in ambient air'. This aspect is very important when considering that cocaine could be easily determined in the frame of the routine activities imposed by the Air Quality Legislation for the monitoring of benzo(a)pyrene. An extensive description of the method applied is presented elsewhere (Cecinato et al., 2009, 2010). Briefly, the composite samples were spiked with deuterated standards and extracted through sonication using a dichloromethane:acetone mixture (4:1 in volume), reduced close to dryness under ultra-pure nitrogen and transferred onto a neutral alumina chromatographic column. Three fractions were collected by eluting with isooctane, isooctane-dichloromethane (3:2) and dichloromethane:acetone (1:1), in sequence. PAHs were in the second fraction while cocaine, nicotine, caffeine, THC, CBL and CBD were in the third (Cecinato et al., 2010).

After solvent evaporation and back dissolution into chloroform, the eluates containing PS were processed through GC-MSD (*Trace GC Ultra* coupled with *Trace DSQ*, both from Thermo Fisher, Rodano, Italy). Glass capillary chromatography was operated in temperature gradient (from 60°C to 280 °C) using a programmed-temperature vaporizer for injection (split-less time 1.25 min). A DBX type column (length = 25 m, i.d. = 0.20 mm, film thickness = 0.25 μm, purchased from Superchrom, Milan, Italy) to obtain the necessary separation of compounds was used. Mass spectrometric detection was operated in selected ion monitoring mode (SIM), using three ion current signals for each analyte and (minimum) two ion traces for the respective internal reference substance (Cecinato et al., 2012). The limits of detection (LODs) of cocaine and cannabinoids were of the order of 0.0003 μg/ml. The entire analytical features of the method was investigated by using the standard addiction method (SAM) (Gonzales and Herrador 2007) on real samples. For this purpose, portions of a homogeneous substrate of atmospheric particulate were fortified with different amount of analytes (three levels of concentrations plus blank, three replicates each level). The overall accuracy was calculated through the differences observed between the pure drug concentrations determined experimentally in the drug fortified samples and those added to them. The accuracy was quantified as 2.3±6.1% for cocaine. The precision was calculated by comparing the analyte concentrations detected in the samples and expressed as percent standard deviation; this

ranged between 4.7% and 6.9% for cocaine but was higher for cannabinoids. For this class, matrix effects and blanks contamination were observed by using SAM and a corresponding increase of uncertainty was observed (accuracy: 13-18%, precision 15-25%). Taking into account the performances of the analytical method and the necessary blank subtraction for cannabinoids the experimental limit of quantifications (LOQs) were defined. Samples analysed in this study were representative of different volumes of air collected. Considering the weekend samples of London, where ~ 55 $m^3$ of air were analysed (the lowest in this study) and the purified extracts were dissolved in 100 μL of solvent for analysis, the limits of quantifications of cocaine and cannabinoids were 0.003 ng/$m^3$ and 0.01 ng/$m^3$, respectively.

12 PAH compounds ranging from benz[a]anthracene (molecular mass = 228.2) up to dibenz[a,h]anthracene (molecular mass = 278.3) were characterized. Considering PAHs, caffeine and nicotine, the LOQs never exceeded 0.01 ng/$m^3$ and the overall accuracy was always better than 20%. Concentrations of $PM_{10}$ in Amsterdam, London and Rome were extracted from publicly available online databases (GGD Amsterdam 2016; London Air Quality Network, 2016; ARPALAZIO, 2016). The values of common meteorological variables (mean and maximum daily temperature, relative humidity, mean and maximum wind speed, precipitation occurrence) were also downloaded from free accessible web sites (Weather Underground, 2016) and are reported in Table S1.

### *2.3 Cocaine and cannabis abuse prevalence in the investigated countries*

According to the latest survey data provided by the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), in the United Kingdom and in Netherlands, drug abuse is widespread. In 2013 in the United Kingdom, the drugs abuse lifetime prevalences of cannabis and cocaine among adults (number of individuals that have experienced the abuse in the age range 15-64 y) were 29.9% and 9.5% respectively. In Netherland the last lifetime data, referring to 2009, report estimates equal to 25.7% and 5.2%, respectively, for the same substances. By contrast in Sweden the illicit drugs abuse looks less common and the lifetime prevalence recorded for cannabis is 14.4%, whereas the last year 15-34y prevalence is in the range 1.1-2%. (EMCDDA, 2015).

## 3. Results and discussion

### *3.1. Concentrations of PAHs, licit and illicit drugs in $PM_{10}$ and $PM_{2.5}$*

$PM_{10}$ was collected in London, while in Amsterdam and Stockholm the PM size fraction changed with the sampling periods and sites. Previous studies show that cocaine and cannabinoids are found in $PM_{2.5}$ with percentages never lower than 75% (Cecinato et al., 2010). To ensure a valid

comparison between countries it was first verified that $PM_{10}$ and $PM_{2.5}$ samples collected simultaneously and at the same site contained similar amounts of PAH and drug substances. Figure 1 illustrates the results for the $PM_{2.5}$ and $PM_{10}$ collected in Amsterdam at A-BG1, the percentages of individual PAH congeners in $PM_{2.5}$ compared to $PM_{10}$ were 89% ± 8%, and the percentages of drugs reached 102% ± 3%. A comparison was not made for cannabinoids due to the absence of these compounds in the samples. Cannabinol distribution was checked in Stockholm and its preponderance in $PM_{2.5}$ was confirmed.

Figure 1.

### *3.2. Psychotropic substances concentrations*

#### 3.2.1. *Amsterdam*

Due to the lack of preliminary information concerning the atmospheric concentrations of illicit drugs in Northern Europe, daily filters collected during March 2011 in Amsterdam were pooled to weekly samples in order to achieve LOQs for the analytical procedure. Table 2A shows the average values of the target compounds measured over the period. The A-BG1 urban background site was the least polluted for all classes. Considering regulated pollutants, small differences in the $PM_{10}$ levels were recorded among the sites (average 36±4 $\mu g/m^3$), by contrast, total PAHs showed larger variations. Total PAHs reached 1.13± 0.06 $ng/m^3$ at A-BG1, whereas they were 80% higher in A-SM1 (2.03 $ng/m^3$) and 50% higher in A-SM2 (1.68 $ng/m^3$). As for the psychotropic substances, caffeine ranged from 0.9 $ng/m^3$ at A-BG1 to 1.2 $ng/m^3$ at A-SM2. More marked differences among sites were observed for nicotine and cocaine. In particular, 0.03 $ng/m^3$ of cocaine and 6.7 ± 0.2 $ng/m^3$ of nicotine were valued at A-BG1 when at A-SM2 these compounds were over 4 times more (0.14 and 30.7 $ng/m^3$ respectively). Intermediate concentrations were measured at A-SM1. Cannabinoid concentrations were all below the quantification limit (< 0.01 $ng/m^3$ for each THC, CBL and CBD).

Table 2.

The concentrations measured in the 2013 campaign are reported in Table 2B. March was the coldest month of the 2013 in Amsterdam (see Table S1), with an average daily temperature of 0°C. This period was also characterized by the presence of rain and snow that could contribute to the decrease of atmospheric PM and nicotine recorded in 2013 compared with 2011. Meanwhile the PAH concentration increased, possibly due to the increased use of domestic heating (Alam et al., 2015).

Atmospheric cocaine variations were not consistent across the sites; a slight increase was observed at A-BG1 and A-SM1 and a drop at A-SM2. The maximum value of cocaine concentration detected in 2013 (0.12 ng/m$^3$) was recorded at A-SM2 (as it was in 2011) together with the peaks of nicotine (20.6 ng/m$^3$) and caffeine (9.1 ng/m$^3$) on 7-8 March. It is worth noting that A-SM2 site was close to a bus stop, and these peaks were probably related to variations in very local sources. Unlike 2011, cannabinol was quantifiable in almost all sites, except at A-BG2; this latter, confirming its feature of urban background, was the less affected by both PS and PAHs.

*3.2.2. London*

Table 3A/B reports the mean PS, PAH and $PM_{10}$ concentrations recorded at L-BG and L-KS during winter and summer seasons. Taking into account both seasons, the concentrations of PM, PAHs and nicotine were higher at L-KS. In particular, in March 2013 the maximum differences between sites were observed for nicotine. In this period at L-KS nicotine reached 27.5 ± 25.5 ng/m$^3$, almost twice the level detected at L-BG (14.3 ± 12.1 ng/m$^3$), even though the variability was large. Less important increases were observed for PAHs and $PM_{10}$. In July 2014 the biggest differences were found for PAHs (1.03 ± 0.24 ng/m$^3$ at L-KS compared to 0.67 ± 0.41 at L-BG), while nicotine and PM at L-KS exceeded 35- 40% of that measured at L-BG. The same behaviour was observed for caffeine that showed the highest mean concentrations at L-KS. This finding confirms that L-KS was, unsurprisingly, more influenced by traffic than L-BG, while the concentration of caffeine and nicotine could depend on peoples' activity in the area, due to its touristic and commercial attractions. By contrast, the maximum amounts of atmospheric cocaine were recorded at L-BG, with average values over the whole campaigns 3-4 times higher than those of L-KS.

The adverse weather conditions that affected the Northern Europe in March 2013 hit also London, with low average temperatures, rain and snow events which were expected to decrease the contaminants in the air. In this context, in London the highest value of cocaine concentration was detected again on 7-8 March (0.33 ng/m$^3$ at L-BG), and average cocaine concentration over the period reached 0.23 ± 0.11 ng/m$^3$ at L-BG and 0.05 ± 0.03 ng/m$^3$ at L-KS. In July, cocaine ranged between 0.18 ± 0.05 ng/m$^3$ at L-BG and 0.06 ± 0.01 ng/m$^3$ at L-KS. Rainy weather accompanied the July 2014 campaign, nonetheless almost all targeted compounds were, on average, more in March than in July. For cocaine, this finding confirms the results of the *Ariadrugs* project where measurements of illicit drugs were carried out weekly over one year. At all the eight cities investigated the lowest concentrations occurred in the summer period (June to August). This trend is not directly connected to any emission reduction, but relates to the increase of dispersion and of boundary layer height during the summer months. The only significant exception to this behaviour

is represented by cannabinol, the sole cannabinoid detected in London. This compound occurred at low but quantifiable concentrations in both seasons and sites (see Table 3). Comparing the sites, cannabinol at L-BG was of the same order of magnitude of that measured at L-KS. Comparing the seasons, the cannabinol behaviour in London was peculiar, because the highest concentration were recorded in July. According to the *Ariadrugs* Project results, in Italy cannabinoids dropped during the summer due to degradation effects induced by solar radiation (Carbone et al., 2010; Cecinato et al., 2012, 2016). The summer increase of atmospheric cannabinol measured in London probably depended on the increase or proximity of drug use.

Table 3.

### *3.2.3 Stockholm*

In Stockholm, due to the low concentrations expected for all chemicals, airborne particulates ($PM_{2.5}$ and $PM_{10}$) were gathered into three composite samples, corresponding to 18 Sep - 1 Oct, 2-15 Oct and 30 Oct - 12 Nov, 2014. The results are summarized in Table 4. Cocaine occurred only at detectable but not quantifiable levels. Cannabinol did not exceed 0.02 $ng/m^3$; meanwhile, the other contaminants occurred at lesser extents than in other cities.

Table 4.

### *3.3.Weekends vs. weekdays atmospheric concentrations*

Various attempts have been made to evaluate differences between weekdays and weekend concentrations of PSs in the atmosphere and to verify if they depended on the weekly trends in drug abuse rate, which are expected to be higher at the weekend. No clear difference was observed, probably due to the impact of atmospheric dispersion, however, the input of special events was detectable. For instance, an increase in cocaine concentration was observed in Rome during the celebration of the White Night Holidays in 2007, and a similar increase in cannabinoid concentrations was found in Barcelona during a massive street protest (Cecinato et al., 2009; Viana et al., 2010; Mastroianni et al., 2015).

Figure 2.

Figure 2 reports the weekend and weekday average concentrations of the investigated compounds (together with the associated variability over the period), measured in London during the sampling campaign carried out in March and July at L-BG (A and B) and L-KS (C and D).

With regard to cocaine, two distinct behaviours were observed. In March, the average concentration of cocaine on weekdays exceeded those measured on weekends both at L-BG and L-KS (though the differences were not statistically significant); the reverse behaviour was observed in July. To illustrate the influence of meteorology and local emission rate on the illegal drug ambient concentrations, the weekend vs. weekdays concentration ratio of cocaine was compared with those of PM and other pollutants (see Table 5).

Table 5.

During March 2013, all substances, except PAHs and caffeine at L-BG, decreased on weekends; the percent decrease of cocaine and PM were very similar at both sites, suggesting that atmospheric dispersion was an important driver of this trend. Thus, the increase of cocaine concentration during the weekdays cannot be associated to the increase of consumption. The reverse was observed in July at L-BG site. There, the cocaine and cannabinol concentrations were higher on weekends, despite the concurrent decrease of PM and other pollutants. In this case, the peculiar behaviour of cocaine could depend on the emission rate in the area, probably associated to consumption, rather than to an increase of population attending at the area. No marked differences were measured at L-KS in July between weekend and weekdays and between cocaine and other pollutants patterns.

In Amsterdam this approach was applicable only with regard to the March 2013 campaign. The particularly adverse meteorological conditions and the consequent strong influence of atmospheric mixing on the pollutant concentrations, combined with the shortness of data series available, hindered any clear observation of possible PS weekly trends. In fact, a widespread reduction in pollutant concentrations was recorded during weekends. The most important decrease was measured for caffeine at A-SM2 (weekend vs weekdays ratio equal to 0.1). This was possibly due to the different habits and number of people at the bus stop close to monitoring site.

### *3.4. Comparison of the contemporary monitoring campaigns*

A monitoring campaign was carried out in Rome from 7 to 27 March 2013, to compare the PS behaviour in the Northern and Southern Europe cities. Also in Rome the measurement period was

375 rainy and cold, which hindered the accumulation of atmospheric pollutants. Figure 3 illustrates the
376 cocaine concentrations, site by site, in each city; the boxplots reported in the Supplementary
377 Material (Figure S1) illustrate the distributions and principal statistical parameters of all
378 concentrations detected in the cities (the A-BG2 sample in Amsterdam was not considered).
379
380 Figure 3.
381
382 Meteorology seems to regulate the general trend of the illicit drug concentrations, although this can
383 be overwhelmed by strong local sources. Analogous conclusions were drawn by Mastroianni et al.
384 (2015) studying 12 sites simultaneously monitored in Barcelona. Comparing the average
385 concentrations measured over the period in London, Amsterdam and Rome, London was the most
386 contaminated city with regards to cocaine, in agreement with the highest levels of abuse associated
387 to the UK (EMCDDA, 2015).
388 The average cocaine concentration calculated over the whole period at both London sites was equal
389 to 0.15±0.11 ng/m$^3$. Slightly higher levels of consumptions are estimated for the Netherlands
390 compared to Italy, however in Amsterdam the mean concentration of cocaine was lower than in
391 Rome, 0.06±0.03 ng/m$^3$ vs. 0.09±0.03.ng/m$^3$. This finding probably depended on the higher
392 population in Rome and the small scale house density at the sites investigated (two or three times
393 higher than the average all over the city for Belloni, Cipro and Francia). This hypothesis is
394 confirmed by the fact that, although the Spanish prevalence of consumption is comparable to that of
395 UK, the average amount of cocaine detected by Mastroianni in the densely populated Barcelona
396 was equal to 0.27 ng/m$^3$. Barcelona population and population density reach 1,600,000 units and
397 15,700 inhabitants/km$^2$, respectively. Another opportunity to compare contemporary data of illicit
398 atmospheric drugs in Northern and Southern Europe was offered by data collected in Amsterdam
399 and eight Italian cities in March 2011. Table 6 reports the cocaine and cannabinoids levels detected
400 in Italy and the features of the sites. Mean cocaine concentration in Amsterdam during 2011
401 reached 0.07± 0.03 ng/m$^3$ and was similar to amounts detected at the urban background site of
402 Milan (Pascal station, located in a public garden) and at the traffic site of Florence, lying in a
403 densely populated city district. Concerning cannabinoids, in Italy only cannabinol was detected in
404 Turin and Palermo, whereas in the other cities most of the investigated cannabinoids occurred at
405 levels above LOQ. Rome showed the highest level of the cannabis active principle THC.
406 Contemporarily cannabinoids were not detected in Amsterdam and, as reported in the text, their
407 concentrations in Northern Europe were in general lower than in Italy even though the consumption

is more widespread there. Our hypothesis is that cannabinoids were consumed more indoors in Northern Europe, or that air ventilation of buildings favoured in Italy resulted in greater emissions.

Table 6.

### *3.5. Comparison of atmospheric cocaine concentrations with wastewater analysis*

Estimates of consumption rates are principally acquired using statistics of crimes or phenomenon related to drugs abuse and population surveys. Relevant uncertainty exists on data produced on this basis due to the difficulties in the acquisition of correct information, as a consequence results produced by different areas are scarcely comparable. However, these tools are very expensive, time consuming and unsuitable for the rapid identification of drug prevalence variations. Illicit substances and their metabolites are excreted by consumers in known percentages, and the characterization of residues in wastewater is currently accepted as a new suitable tool to assess the drug consumption, appearing as a direct and relatively cost effective "measurement" of drug abuse (EMCDDA 2016a).

Though the per capita drug consumption is not deliverable from concentrations in air, the cocaine method used here is a simple extension of procedures adopted for measuring particulate bound PAHs at the regional Air Quality Monitoring networks, and a possible cost-effective tool to index the impact of phenomenon on the territory. In fact cocaine is stable in the atmosphere, and its atmospheric concentration looks less affected than cannabinoids by consumption habits. In this perspective, the comparison with results of measurement performed in wastewater (the sole quantitative method to obtain per capita drug consumption estimates) is crucial to verify whether this is achievable. The present study, together with previous investigations, allowed us to combine the data sets of atmospheric concentrations for the first time at a European level, to correlate atmospheric concentrations of cocaine with the abuse estimates obtained by wastewater analysis for the same year (See Figure 4). When available (2012 and 2013), data were taken from the EMCDDA database (EMCDDA 2016b), otherwise they were collected from literature (Thomas et al., 2011; Zuccato and Castiglioni, 2012; DPA, 2012). Cocaine abuse estimates for Stockholm in 2014 were not available, therefore the wastewater data refer to 2013 (Ort et al., 2014).

Figure 4.

Taking in account all Italian cities, London, Stockholm and Amsterdam in 2013, a good level of correlation was found between the atmospheric concentration of cocaine and the amount of the residues in wastewater ($R^2$= 0.66; p = 0.00131). The $R^2$ value was improved (0.88; p = $1.9828*10^{-5}$) by omitting Turin, where the atmospheric monthly concentration was generated by analysing five daily samples, which reduced the sample representativeness. Poor correlation ($R^2$= 0.22) is obtained by inserting data from Barcelona and Amsterdam 2011. The large differences in the results of wastewater analysis recorded for Amsterdam in 2011 and 2013 do not correspond to the range of variation observed for cocaine in the atmosphere. On the other hand the large amount of cocaine in the air of Barcelona does not fit with daily consumption estimate produced by wastewater analysis for the same year, perhaps due to the high population density in the city.

These findings highlight further limitations of atmospheric measurements to assess the drugs prevalence in the community (in addition to meteorology), that a at much minor extent also belong to the wastewater analysis tool. These are principally due to the large fluctuations in abuse over time, which requires consistent time coverage of the data collected to be mediated, and to the need of an additional tool able to account for local population. (van Nuijs et al., 2011).

The population data is required to normalize the absolute values of illicit substances affecting the atmosphere and wastewater. In this regard, the number of residents is a useful but incomplete parameter because population can widely exceed the resident population due to the daily influx of commuters and visitors, especially in the big cities. Therefore, attempts to define normalization factors are important for both approaches (Cecinato et al., 2013; Bruno et al., 2014).

## Conclusions

This study reports the first European data series of ambient psychotropic substances with the respective geographical and temporal variations, and compares them with the outcomes of wastewater analysis method for assessing population drug consumption. Ambient measurements in Amsterdam, Stockholm and London confirmed the presence of both licit (nicotine, caffeine) and illicit drugs (cocaine, cannabinoids) in the atmosphere and the corresponding concentrations rates were compared with measurements performed in Italian cities. The concentration of PSs were found to vary with both city location and season, which provided the opportunity to investigate geographical and temporal variations in some detail. Among cannabinoids, only cannabinol was detected in the Northern Europe cities. In Amsterdam and London, the cannabis prevalence is reported as higher than in Italy, whilst concentration in air was not. This is likely the result of consumer behavior. Further studies are necessary to clarify this issue but the rate of indoor drug consumption, or the average amount per dose could play a key role. The highest concentrations of

475 cocaine were recorded in London, where the background site investigated was unexpectedly more
476 affected by cocaine than the city centre location. In Stockholm cocaine was not detected in
477 quantifiable amounts (>3 pg/$m^3$). The average concentration detected in March 2011 in Amsterdam
478 was similar to that contemporarily detected in a densely populated area in Florence and in a
479 background site in Milan. A measurement campaign carried out in London, Amsterdam and Rome
480 in March 2013 showed that meteorology was the principal driver of atmospheric cocaine
481 concentrations, but that the inputs of local sources were very relevant. A clear observation of
482 weekly consumption modulation through ambient concentration of illicit drugs was masked by the
483 effect of variations in atmospheric dispersion. This phenomenon could not be controlled for in these
484 short studies, however an attempt was made through comparing the drug concentrations with those
485 of other pollutants. This allowed us to detect a clear weekend-weekday cocaine modulation in July,
486 at one site in London. Further studies are necessary to better understand how meteorology and
487 consumption behavior relate to ambient concentrations of PSs. Nevertheless measuring atmospheric
488 drug concentrations provides a feasible method to capture the differences in drugs consumption
489 between areas and over time. The suitability of this approach to become a tool to index the impact
490 of drug abuse (e.g. cocaine) was investigated by comparing the results of this study to those of the
491 wastewater analysis, routinely used to estimates the consumption prevalence. A good correlation
492 was found when the temporal variability of the consumption and the population were accounted for.
493 Atmospheric measurements of PSs could therefore offer a useful complementary approach to
494 wastewater analysis of PSs, especially where local hot spots need to be identified.

495 References

496 Alam, M.S., Keyte, I.J., Yin J., Stark, C., Jones, A.M., Harrison, R.M., 2015. Diurnal variability of
497 polycyclic aromatic compound (PAC) concentrations: Relationship with meteorological conditions
498 and inferred sources. Atmos. Environ. 122, 427-428.
499
500 Álvarez-Ruiz, R., Andrés-Costa, M.J., Andreu, V., Picó, Y., 2015. Simultaneous determination of
501 traditional and emerging illicit drugs in sediments, sludges and particulate matter. J. Chromatogr. A
502 1405, 103–115.

503 ARPALAZIO, Agenzia Regionale Protezione ambientale del Lazio, 2016,
504 http://www.arpalazio.gov.it/ambiente/aria. (last accessed 09/09/2016).

505 Balducci, C., Nervegna, G., Cecinato, A., 2009. Evaluation of principal cannabinoids in airborne
506 particulates. Anal. Chim. Acta 641, 89–94.

507 Bianchi, F., Bisceglie, F., Dugheri, S., Arcangeli, G., Cupelli, V., del Borrello, E., Sidisky, L.,
508 Careri, M., 2014. Ionic liquid-based solid phase microextraction necklaces for the environmental
509 monitoring of ketamine. J. Chromatogr. A 1331, 1-9.

510 Bruno, R., Hall, W., Kirkbride, P., Yin Lai, F., O'Brien, W., Prichards, J., Thai, P.K., Mueller, J.F.,
511 2014. Commentary on Ort *et al*. (2014):What next to deliver on the promise of large scale sewage-
512 based drug epidemiology? *Addiction* 109, 1353–1354.

513 Carbone, M., Castelluccio, F., Daniele, A., Sutton, A., Ligresti, A., Di Marzo, V., et al., 2010.
514 Chemical characterisation of oxidative degradation products of $\Delta^9$-THC. Tetrahedron 66, 9497-
515 9501.

516 Castiglioni, S., Thomas, K.V., Kasprzyk-Hordern, B., Vandam, L., Griffiths, P., 2014. Testing
517 wastewater to detect illicit drugs: State of the art, potential and research needs. Sci. Total Environ.
518 487, 613–620.

519 Cecinato, A., Balducci, C., 2007. Detection of cocaine in the airborne particles of the Italian cities
520 Rome and Taranto. J. Sep. Sci. 30, 1930–1935.

521 Cecinato, A., Balducci, C., Nervegna, G., 2009. Occurrence of cocaine in the air of the World's
522 cities. An emerging problem? A new tool to investigate the social incidence of drugs? Sci. Total
523 Environ. 407, 1683-1690.

524 Cecinato, A., Balducci, C., Budetta, V., Pasini, A., 2010. Illicit psychotropic substance contents in
525 the air of Italy. Atmos. Environ. 44, 2358-2363.

526 Cecinato, A., Balducci, C., Romagnoli, P., Perilli, M., 2012. Airborne psychotropic substances in
527 eight Italian big cities: Burdens and behaviours. Environ. Pollut. 171, 140-147.

528 Cecinato, A., Balducci, C., Mollica, R., Serpelloni, G., 2013. Social [and health] relevance of
529 psychotropic substances monitoring in air. Environ. Pollut. 179, 27-32.

530 Cecinato, A., Balducci, C., Romagnoli, P., Perilli, M., 2014. Behaviours of psychotropic substances
531 in indoor and outdoor environments of Rome, Italy. Environ. Sci. Pollut. Res. 21, 9193–9200.

532 Cecinato, A., Balducci, C., Perilli, M., 2016. Illicit psychotropic substances in the air: the state-of-
533 art. Sci. Total Environ. 539, 1-6.

534 Daughton, C.G., 2011. Illicit drugs: contaminants in the environment and utility in forensic
535 epidemiology. Rev. Environ. Contam. Toxicol. 210, 59-110.

536 De Giorgio, F., Strano Rossi, S., Rainio, J., Chiarotti, M., 2004. Cocaine found in a child's hair due
537 to environmental exposure?. Int. J. Legal Med. 118, 310-312.

538 DPA. Department for Anti-drug Policies of the Presidency of Ministers' Council of Italy, 2012.
539 Annual Report to Parliament. Available from:
540 http://www.politicheantidroga.gov.it/attivita/pubblicazioni/relazioni-al-parlamento/relazione-
541 annuale-2012/presentazione.aspx (last accessed 09/09/2016).

542 European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), 2015. European Drug
543 Report, trends and developments. Luxembourg: Publications Office of the European Union.
544 http://www.emcdda.europa.eu./publications/edr/trends-developments/2015 (last accessed
545 09/09/2016).

546 European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), 2016a. Assessing illicit
547 drugs in wastewater: advances in wastewater-based drug epidemiology, Insights 22, Publications
548 Office of the European Union, Luxembourg. ISBN 978-92-9168-856-2.

549 European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), 2016b. Wastewater
550 analysis and drugs - a European multi-city study. http://www.emcdda.europa.eu/topics/pods/waste-
551 water-analysis. (last accessed 09/09/2016).

552 Garcia-Bournissen, F., Nesterenko, M., Karaskov, T., Koren, G. 2009. Passive environmental
553 exposure to cocaine in Canadian children. Pediatr. Drug. 11, 30-32.Gidhagen, L., Johansson, C.,
554 Ström, J., Kristensson, A., Swietlicki, E., and Pirjola, L., 2003. Model simulation of ultrafine
555 particles inside a road tunnel. Atmospheric Environment, 37, 2023-2036.

556 Gonzales, A.G., Herrador, M.A., 2007. A practical guide to analytical method validation, including
557 measurement uncertainty and accuracy profiles. Trends Anal. Chem. 26, 227–38.

558 Hannigan, M.P., Cass, G.R., Penman, B.W., Crespi, C.L., Lafleur, A.L., Busby Jr., W.F., et al.,
559 1998. Bioassay-directed chemical analysis of Los Angeles airborne particulate matter using a
560 human cell mutagenicity assay. Environ. Sci. Technol. 32, 3502–3514.

561 Hu, D., Chen, J., Ye, X., Li, L., Yang, X., 2011. Hygroscopicity and evaporation of ammonium
562 chloride and ammonium nitrate: Relative humidity and size effects on the growth factor.
563 Atmospheric Environment 45, 2349-2355.

564 Huerta-Fontela, M., Galceran, M.T., Ventura, F., 2008. Stimulatory drugs of abuse in surface waters
565 and their removal in a conventional drinking water treatment plant. Environ. Sci. Technol. 42,
566 6809-6816.

567 Johansson, C., Burman, L., Forsberg, B. 2009. The effects of congestions tax on air quality and
568 health. Atmos. Environ. 43, 4843-4854.

569 Kelly, J.T., Baker, K.R., Nolte, C.G., Napelenok, S.L., Keene, W.C., Pszenny, A.A.P., 2016.
570 Simulating the phase partitioning of NH3, HNO3, and HCl with size-resolved particles over
571 northern Colorado in winter. Atmospheric Environment 131, 67-77.

572 Kidwell, D.A., Blanco, M.A., Smith, F.P., 1997 Cocaine detection in a university population by hair
573 analysis and skin swab testing. Forensic Sci. Int. 84, 75-86.

574 Ladji, R., Yassaa, N., Balducci, C., Cecinato, A., Meklati, B.Y., 2009 Annual variation of
575 particulate organic compounds in PM10 in the urban atmosphere of Algiers. Atmos. Res. 9, 258-
576 269.

577 London Air Quality Network, 2016. www.londonair.org.uk. ( last accessed 09/09/2016).

578 Mastroianni, N., Postigo, C., De Alda, M.L., Barcelo, D., 2013. Illicit and abused drugs in sewage
579 sludge: Method optimization and occurrence. J. Chromatogr. A. 1332, 29-37.

580 Mastroianni, N., Postigo, C., De Alda, M. L., Viana, M., Rodríguez, A., Alastuey, A., Querol, X.,
581 Barceló, D., 2015. Comprehensive monitoring of the occurrence of 22 drugs of abuse and
582 transformation products in airborne particulate matter in the city of Barcelona. Sci. Total Environ.
583 532, 344–352.

584 McKenzie, E. J., , Miskelly, G.M., Butler, P. A. G., 2013. Detection of methamphetamine in
585 indoor air using dynamic solid phase microextraction: a supplementary method to surface wipe
586 sampling. Anal. Method. 5, 5418- 5424.

587 Moussaoui, Y.,Balducci, C., Cecinato, A., Meklati, B.Y., 2013. Atmospheric particulate organic
588 matter at urbanand forest sites of Northern Algeria. Urban Clim. 4, 85-101.

589 Ort, C., van Nuijs, A. L. N., Berset, J.D., Bijlsma, L., Castiglioni, S., Covaci A., de Voogt, P, et al.,
590 2014. Spatial differences and temporal changes in illicit drug use in Europe quantified by
591 wastewater analysis. Addiction 109, 1338–1352.

592 Perrino, C., Pietrodangelo, A., Febo, A., 2001. An atmospheric stability index based on radon
593 progeny measurements for the evaluation of primary urban pollution. Atmos. Environ. 35,5235–
594 5344.

595 Pichini, S., Garcia-Algar, O., Alvarez, A., Gottardi M., Marchei, E., Svaizer F., Pellegrini, M.,
596 Rotolo, M.C., Pacifici, R., 2014. Assessment of unsuspected exposure to drugs of abuse in children
597 from a Mediterranean City by hair testing. Int. J. Environ. Res. Public Health. 11, 2288–2298.

598 Postigo, C., Lopez de Alda, M.J., Viana, M., Querol, X., Alastuey, A., et al., 2009. Determination
599 of drugs of abuse in airborne particles by pressurized liquid extraction and liquid chromatography-
600 electrospray-tandem mass spectrometry. Anal. Chem. 81, 4382–4388.

601 Romagnoli, P., Balducci, C., Perilli, M., Gherardi, M., Gordiani, A., et al. Indoor PAHs at schools,
602 homes and offices in Rome, Italy. Atmos. Environ. 92, 51-59, 2014.

603 Seabra Pereira, C.D., Luciane, A., Maranho, L.A., Cortez, F.S. , Pusceddu, F.H., Santos, A.R.,
604 Ribeiro, et al.,. 2016. Occurrence of pharmaceuticals and cocaine in a Brazilian coastal zone. Sci.
605 Total Environ. 548–549, 148–154.

606 GGD Amsterdam, Air Quality Monitoring Network, https://www.luchtmeetnet.nl. (last accessed
607 09/09/2016).

608 Thomas, K. V., Bijlsma, L., Castiglioni, S., Covaci, A., Emke, E., Grabic, R., Hernández, F., et al.,
609 2012. Comparing illicit drugs use in 19 European cities through sewage analysis. Sci. Total
610 Environ. 432, 432–439.

611 van der Aa, M., Bijlsma, L., Emke E. , Dijkman E. , van Nuijs A.L.N., van de Ven B. , Hernández
612 F. , et al., 2013. Risk assessment for drugs of abuse in the Dutch watercycle. Water Res. 47, 1848-
613 1857.

614 van Nuijs, A.L.N., Castiglioni, S.,Tarcomnicu, I., Postigo, C., Lopez de Alda, M., Neels, H., et al.,
615 2011. Illicit drug consumption estimations derived from wastewater analysis: A critical review. Sci.
616 Total Environ. 409, 3564–3577.

617 Viana, M., Querol, X., Alastuey, A., Postigo, C., López de Alda, M.J., et al., 2010. Drugs of abuse
618 in airborne particulates in urban environments. Environ. Internat. 36, 527–534.

619 Viana, M., Postigo, C., Querol, X., Alastuey, A., Lopez de Alda, M.J., et al., 2011. Cocaine and
620 other illicit drugs in airborne particulates in urban environments: A reflection of social conduct and
621 population size. Environ. Pollut. 159, 1241-1247.

622 Weather Underground 2016. https://www.wunderground.com/history/ (last accessed 09/09/2016)

623 Zuccato, E., Castiglioni S., 2012. Consumi di sostanze stupefacenti nelle città europee
624 Ricerca&Pratica 28, 252-260.

625 Zuccato, E., Chiabrando, C., Castiglioni, S., Calamari, D., Bagnati R., Schiarea, S., Fanelli, R.,
626 2005. Cocaine in surface waters: a new evidence-based tool to monitor community drug abuse.
627 Environ. Health Perspect. 5, 14.
628
629

**Table headings**

Table 1. Population rate and density of the cities investigated. PM fraction sampled, sampling dates and typology of the monitoring sites in each city.
Symbols adopted for sites: BG = urban background; KS= kerbside; SM= street monitoring.

Table 2. Average concentrations of nicotine (NIC), caffeine (CAF), cocaine (COC), polycyclic aromatic hydrocarbons (PAH), $PM_{10}$ and cannabinol (CBL) in the atmosphere of Amsterdam. A) 9-16 March 2011; B) 7-27 March 2013. na: not available.
$^{(*)}$ Sampling limited to 23– 24 March.

Table 3. Average concentrations of nicotine, caffeine, cocaine, cannabinol, polycyclic aromatic hydrocarbons and $PM_{10}$ in the atmosphere of London A) 7-27 March 2013; B) 10-22 July 2014. For compound symbols see Table 2

Table 4. Average concentrations of nicotine, caffeine, cocaine, cannabinol and polycyclic aromatic hydrocarbons in the atmosphere of Stockholm. For compound symbols see Table 2

Table 5. Ratios of weekend vs. weekdays pollutants concentrations recorded in London in March 2013 and July 2014 and in Amsterdam in March 2013.

Table 6. Concentrations of cocaine (COC), cannabinol (CBL), $\Delta^9$-tetrahydrocannabinol (THC) and cannabidiol (CBL) detected in 8 Italian cities in March 2011. Population, population density and sites typology. TR= traffic site, BG= urban background.

Table S1. Mean values of average ($T_{ave}$) and maximum ($T_{max}$) daily temperature, relative humidity (RH), barometric pressure (P), precipitation days (%), maximum ($w_{max}$) and minimum ($w_{min}$) daily wind speed, and prevailing wind direction ($w_{dir}$) in London, Amsterdam and Rome. 7-27 March, 2013.

660 **Figure captions**

661

662 Figure 1. $PM_{2.5}/PM_{10}$ concentration ratio of polycyclic aromatic hydrocarbons and psychotropic
663 substances. Amsterdam, A-BG1 station, 9-16 March 2011.
664 Symbols: BaA = benz[a]anthracene; BbF = benzo[b]fluoranthene; BjF = benzo[j]fluoranthene; BkF
665 = benzo[k]fluoranthene; BaP = benzo[a]pyrene; IP = indeno[1,2,3-cd]pyrene; DBA = dibenz[a,h]
666 anthracene; BPE = benzo[ghi]perylene; NIC = nicotine; CAF = caffeine; COC = cocaine.

667

668 Figure 2. Weekends and weekdays average concentrations valuated in March and July at L-BG (A
669 and B) and L-KS (C and D) and associated variability of the concentrations over the periods. $PM_{10}$
670 are given in $\mu g/m^3$ units, all other chemicals in $ng/m^3$.
671 Symbols: NIC = nicotine; CAF = caffeine; COC = cocaine; CBL = cannabinol.

672

673 Figure 3. Cocaine concentrations detected in London, Amsterdam and Rome. Sampling period 7-27
674 March 2013.

675

676 Figure 4. Average aerial concentration of cocaine in European cities and estimates of the drugs
677 abuse produced by wastewater analysis in the same year.

678

679 Figure S1. Box plots reporting values of cocaine concentrations recorded in London, Amsterdam
680 and Rome in March 2013. Box boundaries represents 25 and 75 percentiles, the average is indicated
681 with the dotted line, median with continuous line. Whiskers represent minimum and maximum.

**Table(s)**

| city | population | population density | Site symbols | site type | PM fraction | sampling period |
|---|---|---|---|---|---|---|
| Amsterdam | 820000 | 4892 | A-BG1 | BG | 10-2.5 | 9-16/03/2011 |
| | | | A-SM1 | SM | 2.5 | 7-27/03/2013 |
| | | | A-SM2 | SM | 10 | |
| | | | A-BG2 | BG | 10 | 23-24/03/2013 |
| London | 8538689 | 5432 | L-BG | BG | 10 | 7-27/03/2013 |
| | | | L-KS | KS | 10 | 10-22/07/2014 |
| Stockholm | 912000 | 4872 | S-BG | BG | 10-2.5 | 18/09-15/10/2014 30/10-12/11/2014 |
| Rome | 2761477 | 2231 | Francia (FR) | SM | 10 | 7-27/03/2013 |
| | | | Belloni (BE) | BG | 10 | |
| | | | Cipro (CI) | BG | 10 | |
| | | | Villa Ada (VA) | BG | 10 | |

Table 1. Population rate and density of the cities investigated. PM fraction sampled, sampling dates and typology of the monitoring sites in each city.

Symbols adopted for sites: BG = urban background; KS= kerbside; SM= street monitoring.

**Table(s)**

| **A. March 2011** | A-BG1 | A-SM1 | A-SM2 | A-BG2 |
|---|---|---|---|---|
| n. of samples | 2 | 1 | 1 | na |
| NIC, ng/m$^3$ | 6.7 ± 0.2 | 8.4 | 30.7 | na |
| CAF, ng/m$^3$ | 0.80 ± 0.01 | 0.9 | 1.2 | na |
| CBL, ng/m$^3$ | <0.01 | <0.01 | <0.01 | na |
| COC, ng/m$^3$ | 0.03 ± 0.00 | 0.06 | 0.14 | na |
| PAH, ng/m$^3$ | 1.13 ± 0.06 | 2.03 | 1.68 | na |
| $PM_{10}$, µg/m$^3$ | 32 | 36 | 40 | na |
| **B. March 2013** | A-BG1 | A-SM1 | A-SM2 | A-BG2* |
| n. of samples | 4 | 3 | 7 | 1 |
| NIC, ng/m$^3$ | 5.4 ± 3.0 | 3.5 ± 2.0 | 12.5 ± 5.3 | 0.4 |
| CAF, ng/m$^3$ | 0.18 ± 0.11 | 0.21 ± 0.17 | 2.21 ± 3.42 | 0.06 |
| COC, ng/m$^3$ | 0.05 ± 0.02 | 0.07 ± 0.05 | 0.06 ± 0.04 | < 0.003 |
| CBL, ng/m$^3$ | 0.02 ± 0.01 | 0.01 ± 0.00 | 0.03 ± 0.03 | < 0.003 |
| PAH, ng/m$^3$ | 3.11 ± 0.93 | 3.01 ± 2.26 | 2.92 ± 1.06 | 2.56 |
| $PM_{10}$, µg/m$^3$ | 27 ± 11 | 30 ± 6 | 26 ± 17 | na |

Table 2. Average concentrations of nicotine (NIC), caffeine (CAF), cocaine (COC), polycyclic aromatic hydrocarbons (PAH), $PM_{10}$ and cannabinol (CBL) in the atmosphere of Amsterdam. A) 9-16 March 2011; B) 7-27 March 2013. na: not available.

$^{(*)}$ Sampling limited to 23– 24 March.

**Table(s)**

| **A. March 2013** | L-BG | L-KS |
|---|---|---|
| n. of samples | 7 | 5 |
| NIC, ng/m$^3$ | 14.3 ± 12.1 | 27,5 ± 25.5 |
| CAF, ng/m$^3$ | 0.59± 0.30 | 0.65 ± 0.31 |
| COC, ng/m$^3$ | 0.23 ± 0.11 | 0.05 ± 0.03 |
| CBL, ng/m$^3$ | 0.02 ± 0.02 | 0.01 ± 0.01 |
| PAH, ng/m$^3$ | 1.93 ± 1.04 | 2.24 ± 0.4 |
| $PM_{10}$, µg/m$^3$ | 28 ± 11 | 35 ± 12 |
| **B. July 2014** | L-BG | L-KS |
| n. of samples | 5 | 5 |
| NIC, ng/m$^3$ | 20.6 ± 13.3 | 27.0 ± 7.3 |
| CAF, ng/m$^3$ | 0.45± 0.14 | 0.47 ± 0.17 |
| COC, ng/m$^3$ | 0.18 ± 0.05 | 0.06 ± 0.01 |
| CBL, ng/m$^3$ | 0.06 ± 0.02 | 0.05 ± 0.02 |
| PAH, ng/m$^3$ | 0.67 ± 0.41 | 1.03 ± 0.24 |
| $PM_{10}$, µg/m$^3$ | 17 ± 3 | 24 ± 6 |

Table 3. Average concentrations of nicotine, caffeine, cocaine, cannabinol, polycyclic aromatic hydrocarbons and $PM_{10}$ in the atmosphere of London A) 7-27 March 2013; B) 10-22 July 2014. For compound symbols see Table 2

**Table(s)**

| period | 18 Sep - 1 Oct | 2 - 15 Oct | 30 Oct - 12 Nov |
|---|---|---|---|
| n. of samples | 2 | 1 | 2 |
| NIC, ng/$m^3$ | 3.5 ± 0.1 | 3.4 | 4.4± 0.2 |
| CAF, ng/$m^3$ | 0.48 ± 0.03 | 0.20 | 0.08± 0.01 |
| COC, ng/$m^3$ | < 0.003 | < 0.003 | < 0.003 |
| CBL, ng/$m^3$ | 0.02 ± 0.00 | 0.02 | < 0.01 |
| PAH, ng/$m^3$ | 0.28 ± 0.02 | 0.46 | 0.47± 0.03 |

Table 4. Average concentrations of nicotine, caffeine, cocaine, cannabinol and polycyclic aromatic hydrocarbons in the atmosphere of Stockholm. For compound symbols see Table 2

**Table(s)**

| weekends vs. weekdays | London | | | | Amsterdam | |
|---|---|---|---|---|---|---|
| | March | | July | | March | |
| | L-BG | L-KS | L-BG | L-KS | A-BG1 | A-SM2 |
| $PM_{10}$ | 0.9 | 0.7 | 0.9 | 1.2 | 0.8 | 0.6 |
| PAHs | 1.3 | 0.9 | 0.7 | 1.1 | 1.4 | 0.7 |
| NIC | 1.0 | 0.6 | 0.8 | 0.8 | 0.4 | 0.6 |
| CAF | 1.4 | 0.6 | 0.8 | 1.8 | 0.5 | 0.1 |
| COC | 0.9 | 0.7 | 1.4 | 1.1 | 0.8 | 0.4 |
| CBL | nd | nd | 1.1 | 0.9 | 1.1 | 1.5 |

Table 5. Ratios of weekend vs. weekdays pollutant concentrations recorded in London in March 2013 and July 2014 and in Amsterdam in March 2013.

**Table(s)**

| | Population | Population density | Site | Site type | COC | CBL | THC | CBD |
|---|---|---|---|---|---|---|---|---|
| **Turin** | **907563** | **6972** | **Via della Consolata** | **TR** | **0.19** | **0.02** | **<0.005** | **<0.005** |
| **Milan** | **1324110** | **7363** | **Via Pascal** | **BG** | **0.07 ± 0.03** | **0.03 ± 0.01** | **<0.005** | **0.04 ± 0.06** |
| **Verona** | **263964** | **1308** | **Via Dominutti** | **BG** | **0.05 ± 0.02** | **0.02 ± 0.01** | **0.02 ± 0.02** | **<0.005** |
| **Bologna** | **380181** | **2701** | **Porta San Felice** | **TR** | **0.06** | **0.08** | **0.03** | **0.01** |
| **Florence** | **371282** | **3625** | **Via Ponte alle Mosse** | **TR** | **0.07 ± 0.03** | **0.09 ± 0.04** | **0.02 ± 0.02** | **0.10 ± 0.09** |
| **Rome** | **2761477** | **2231** | **Cinecittà** | **BG** | **0.14 ± 0.04** | **0.12 ± 0.07** | **0.05 ± 0.06** | **0.12 ± 0.15** |
| **Naples** | **959574** | **8226** | **Via Metastasio** | **TR** | **0.13 ± 0.05** | **0.09 ± 0.07** | **0.04 ± 0.03** | **0.16 ± 0.08** |
| **Palermo** | **655875** | **4128** | **Via dei Cappuccini** | **BG** | **0.02 ± 0.01** | **0.01 ± 0.01** | **<0.005** | **<0.005** |

Table 6. Concentrations of cocaine (COC), cannabinol (CBL), $\Delta^9$-tetrahydrocannabinol (THC) and cannabidiol (CBL) detected in 8 Italian cities in March 2011. Population, population density and sites typology. TR= traffic site, BG= urban background.

**Figure(s)**

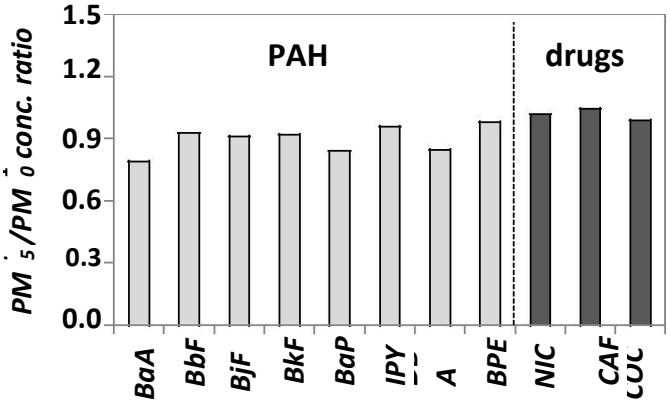


Figure 1. $PM_{2.5}/PM_{10}$ concentration ratio of polycyclic aromatic hydrocarbons and psychotropic substances. Amsterdam, A-BG1 station, 9-16 March 2011.

Symbols: BaA = benz[a]anthracene; BbF = benzo[b]fluoranthene; BjF = benzo[j]fluoranthene; BkF = benzo[k]fluoranthene; BaP = benzo[a]pyrene; IP = indeno[1,2,3-cd]pyrene; DBA = dibenz[a,h]anthracene; BPE = benzo[ghi]perylene; NIC = nicotine; CAF = caffeine; COC = cocaine.

**Figure(s)**

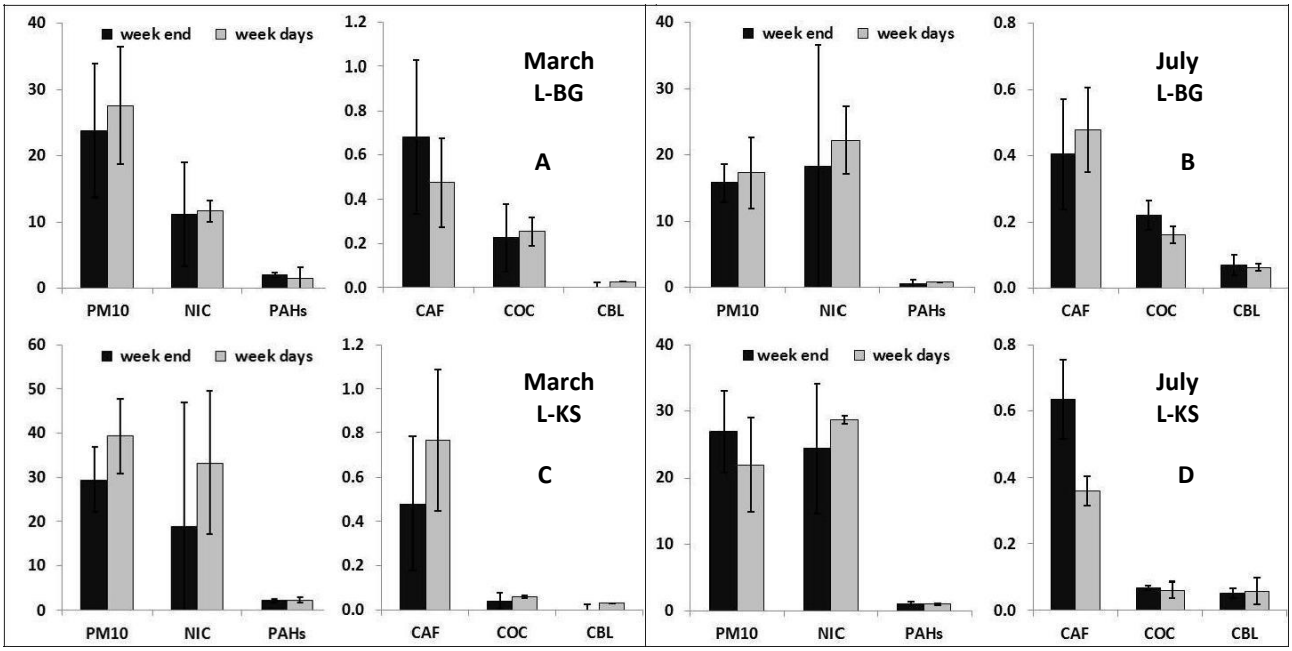


Figure 2. Weekends and weekdays average concentrations valuated in March and July at L-BG (A and B) and L-KS (C and D) and associated variability of the concentrations over the periods. $PM_{10}$ are given in $\mu g/m^3$ units, all other chemicals in $ng/m^3$.

Symbols: NIC = nicotine; CAF = caffeine; COC = cocaine; CBL = cannabinol.

**Figure(s)**

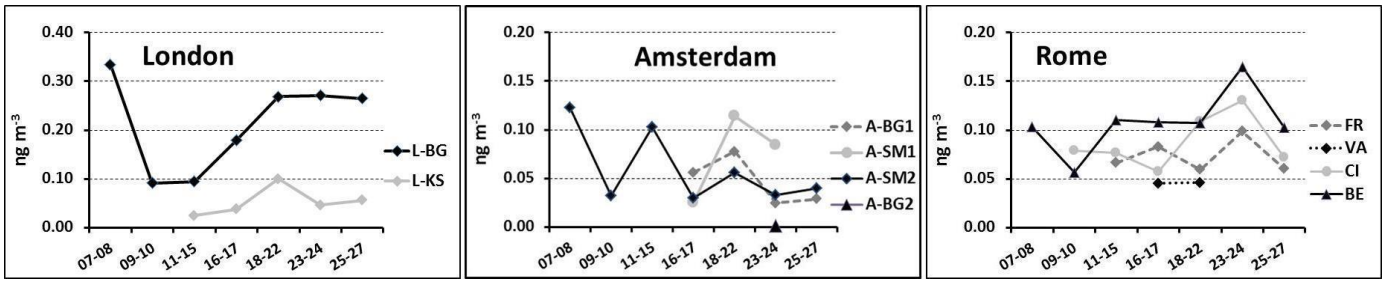


Figure 3. Cocaine concentrations detected in London, Amsterdam and Rome. Sampling period 7-27